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THE USE OF PAN FOR AN EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF ZINC IN THE PRESENCE OF GREAT EXCESSES OF CADMIUM OR LEAD

A THESIS

Presented to

The Faculty of the Graduate Division

by

Roger Harvey Weiss

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

Georgia Institute of Technology

August, 1968

THE USE OF PAN FOR AN EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF ZINC IN THE PRESENCE OF GREAT EXCESSES OF CADMIUM OR LEAD

Approved:

Chairman

Date approved by Chairman: Nov. 8. 68

ACKNOWLEDGMENTS

It is a pleasure to acknowledge my indebtedness to Dr. H. A. Flaschka for his guidance, inspiration and friendship. He never failed to amaze me with his vast store of knowledge of analytical chemistry and each discussion with him enriched me. Dr. P. E. Sturrock, and Dr. H. R. Hunt provided generous assistance during the preparation of the manuscript and in other ways as well.

A portion of this work was supported by Humboldt State College of Arcata, California in the form of a sabbatical leave. The remainder of this work was performed under a National Science Foundation Science Faculty Fellowship. I wish to thank both organizations for their generous aid. I am also indebted to Dr. W. M. Spicer for obtaining a waiver of out-of-state tuition for me for one year at Georgia Tech.

A number of my laboratory coworkers in Dr. Flaschka's group, particularly Drs. J. Butcher, J. Garrett and R. Speights and Mr. J. Mann, were helpful in providing advice and encouragement.

Finally, I am especially grateful to my wife, Anne, for her encouragement, patience and support during this endeavor.

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SUMMARY

Several sensitive, highly selective and rugged photometric procedures applicable to the determination of zinc in high purity cadmium and cadmium salts have been developed. The approach used throughout includes:

1. Partial masking of cadmium against PAN by the addition of a large quantity of potassium iodide. This allows the zinc to compete successfully for PAN in the presence of a great excess of cadmium.
2. Maintaining a sufficiently high pH (about 7) to permit the complete conversion of zinc to its PAN complexes. A maleic acid-maleate buffer is used.
3. Adding PAN in increments. This makes possible the complete conversion of zinc to its PAN complexes despite the rapid precipitation of free PAN.
4. Extracting the red zinc panates with chloroform. Cadmium panates rapidly decompose with the simultaneous backtransfer of cadmium to the aqueous phase.

In a number of the operations the desired results are obtained by taking advantage of favorable kinetics rather than by reaching equilibrium.

The sensitivity of the basic procedure is about 0.5 μg of zinc and the limiting cadmium to zinc molar ratio is about 100,000:1. Slightly modified procedures allow as much as a fivefold increase in the limiting ratio.

The tolerance limits of all anions of commercially important cadmium salts and of all cations commonly encountered as impurities in cadmium are found to be sufficiently high to permit the application of the procedures to cadmium samples of only moderate purity. The high tolerance limits for cations are due, in part, to an unusual and important type of masking which occurs in this system. The great excess of cadmium is only partially masked against PAN by iodide hence it serves as a PAN "sink" thereby masking PAN against other cations.

The tolerance limits of a number of cations can be increased by the addition of a suitably greater amount of cyanide than specified in the basic procedure. A trial and error procedure using the formation of the very inert green cobalt(III) panate as an indicator allows the determination of the appropriate amount of cyanide in such cases.

The approach developed for the cadmium systems has been found to be also applicable to lead systems. The principal difference between the two systems is that the lead panates do not undergo decomposition within a reasonable time in the course of a chloroform extraction. Thus lead has to be fully masked against PAN by iodide. The basic procedure for the lead system has about the same sensitivity and limiting molar ratio as the cadmium basic procedure. Some modifications allow up to a threefold increase in the limiting ratio. The tolerance limits for interferences are, in almost all cases, lower in the lead system than in the cadmium system but are still adequate to handle even moderately high purity lead and lead salt samples.

Superficial observations indicate that the approach is also feasible for the determination of zinc in high purity copper, mercury or sil-

ver. Under the conditions that were used for the observations the limiting molar ratios are 50,000:1, 500,000:1, and 250,000:1, respectively for the three metals named above.

CHAPTER I

THE DETERMINATION OF ZINC IN THE PRESENCE OF GREAT EXCESSES OF CADMIUM

1. Survey of the Present Status of the Problem

Since cadmium and its compounds always contain some zinc and since the chemical properties of these elements are quite similar, the determination of zinc in the presence of a great excess of cadmium is a problem of practical importance and considerable difficulty.

Cadmium is most commonly found in nature in low concentration in association with zinc. No cadmium or cadmium compounds are produced other than the small amounts obtained from the refining of the commercially important carbonate and sulfide ores of zinc. As a first step toward winning the metals these ores are roasted to the oxide. In the principal metallurgical process the oxide is reduced with coke, and then zinc and cadmium are distilled. Cadmium (b.p. 767°C) and zinc (b.p. 907°C) can be separated by fractional distillation. However as zinc is the major constituent and cadmium the minor one, any cadmium so produced is contaminated to a greater or lesser extent by zinc. An alternative megallurgical process for zinc involves dissolving the oxide in a suitable acid followed by cathodic electrodeposition of the zinc. Zinc dust is added prior to the electrolysis to reduce the cadmium ions and precipitate cadmium. The standard potentials of the two redox couples which differ by 0.36 volts would be expected to permit an excellent separation. However, in practice, the quality of the separation depends on the actual rather than the

standard potential difference. Operating conditions, including bath temperature, ionic strength and the presence of complexing agents, result in an actual potential difference significantly less than 0.36 volts. Consequently the zinc dust reduction also does not produce zinc-free cadmium. In fact, even though further purification steps follow, the best grades of cadmium and cadmium compounds which are readily available contain from 10^{-2} to 10^{-5} weight-weight per cent zinc.

Presently there is no method available which combines reasonable speed with good accuracy, uses commonly available and inexpensive equipment and is sufficiently sensitive to determine zinc in cadmium even at 10^{-2} per cent level. The lack of such a method was of no consequence until a few years ago, as the presence of trace quantities of zinc did not adversely affect those properties of cadmium which are pertinent to its various uses. Recently there has developed an area of science involving the study of the properties of extremely pure materials as well as a whole new technology dependent on such materials. Concurrently and for obvious reasons, trace analysis has become a major concern of analytical chemistry. In the light of current needs, and anticipating the needs of the near future, there is reason to develop a method for determining traces of zinc in cadmium at this time.

The determination of zinc in the presence of cadmium is, per se, troublesome due to the great similarity in the chemical properties of these elements. When applied to the analysis of high purity cadmium the inherent difficulty of this determination is enhanced by an added constraint, namely, the extremely high cadmium to zinc ratio. Many conceivable methods fail for one reason or another; for example, polarography

which cannot be applied because the wave of cadmium precedes that of zinc and flame emission spectrophotometry which is not sufficiently sensitive. Some of the better existing methods are described below, along with the reasons why they fail to meet the above mentioned criteria for a good method for determinations on a trace level.

Lingane *(1)* reports a method involving stripping of cadmium into a mercury cathode at controlled potential followed by a polarographic determination of zinc in the essentially cadmium-free solution. The time required for the electrolytic stripping separation of cadmium from a large sample is a serious handicap to this procedure, particularly if a suitable potentiostat is not available.

Conventional spectrography and radio-frequency spark sources mass spectrography can be used for this determination but leave much to be desired in so far as accuracy is concerned. The high cost and great rarity of rf spark source mass spectrographs as well as the time required are severe limitations to the general applicability of that method.

Neutron activation analysis may be employed if fast neutrons are used. The disadvantages are similar to those of rf spark mass spectrography and, in addition, chemical separation steps are required.

Winefordner *(2)* reports the determination of nanogram quantities of zinc by atomic flame fluorescence, using the resonance line of zinc at 213.9 mμ. If large quantities of other salts are present, however, difficulties arise due to burner clogging. Precision, accuracy and selectivity are similar to those of other types of flame photometry. The nonexistence of general purpose commercial instruments for this method is a great disadvantage.

Fluorimetry has been used by Trenholm and Ryan *(3)* to determine zinc in cadmium with cadmium to zinc molar ratios as high as 4000:1. Excellent precision and good accuracy have been attained. The extreme dependence of fluorimetry on experimental conditions is a disadvantage of this method. Furthermore, fluorimeters, although now widely available in laboratories, are still less commonly found than visible range spectrophotometers. Most importantly, the sensitivity of this method is at least an order of magnitude too low to be useful in trace analysis.

Flaschka and Butcher *(4)* report a photometric titration using DTPA as the titrant, xylenol orange as the metallochromic indicator for zinc and a high iodide concentration to selectivity mask the cadmium. By this procedure it was possible to determine zinc in cadmium provided the cadmium to zinc molar ratio was not more than 3300:1. The prime defect of this method is the lack of sufficient sensitivity.

The best of the present methods is atomic absorption flame spectrophotometry. Burner clogging problems arise only at a molar cadmium to zinc ratio of more than 300,000:1. The method is rapid, very sensitive and reasonably accurate. Its only drawback is the lack of widespread availability of atomic absorption flame spectrophotometers, but that situation is changing rapidly.

Nevertheless, a procedure for determining zinc in presence of a ten thousandfold or greater molar excess of cadmium using only commonly available equipment would be valuable now, and retain future value as an alternate method.

Addendum

The preceding survey reports the situation existing when the work

described here was begun. However, in view of the need for a good method for determining zinc in high purity cadmium it is not surprising that other investigators are also working in this field. Just prior to the completion of the work described here two papers, or, more correctly, a paper and an abstract of a paper, presenting new methods became available. These methods are totally different from those reported in this work, and only one of them might be considered a good method.

Zhivopistsev and coworkers *(5)* describe a photometric method that is capable of handling samples having a cadmium to zinc molar ratio of 60,000:1. The procedure is lengthy and complicated. Some of the necessary solutions have a rather limited shelf life and the chromogenic agent, 4-dimethylaminophenyl-4'-methylbenzoaminophenylantipyrylcarbinol, is not commercially available.

Selezneva and Bragina *(6)* two coworkers of Zhivopistsev, have developed a photometric method using rhodamine B as the chromogenic agent. The original paper was not available and the abstract fails to report the maximum cadmium to zinc molar ratio that can be dealt with. A reasonable surmise is that the method may be applicable to samples having molar ratios up to 500,000:1. The method appears to be a good one although this evaluation is tentative since it is based on the contents of an abstract only.

2. Attempts at a Photometric Titration of Zinc

A study directed toward the development of a photometric titration for traces of zinc in cadmium was initiated. Such a procedure would use iodide to mask cadmium, and employ as the titrant a dye which commonly

serves as a metallochromic indicator for zinc.

2.1. Investigations Using Xylenol Orange

Flaschka and Butcher *(4)* found that, at a suitable pH, a high concentration of iodide prevents the formation of the red cadmium-xylenol orange (XO) complex but does not prevent the formation of the red zinc-XO complex. These facts suggest that a photometric titration procedure for the determination of zinc in the presence of cadmium would be possible using XO as the titrant. It was known that the red zinc-XO complex begins to form only at pH value above about 4 while at a pH above 5.5 free XO begins to change color from yellow to red. This changing of the color of the free dye from yellow to red sets an upper limit to the useful pH region; advantageous use cannot be made of the expected increase in the conditional constant for the formation of the zinc-XO complex with increases in pH. Attempts were made at the photometric titration of zinc with XO, in solutions free of both cadmium and iodide, and in solutions containing iodide but no cadmium. The pH range from 4.5 to 6.3 was investigated, with the pH being maintained by acetate or phthalate buffers. In all cases curves rather than straight line segments were obtained when the absorbance (at 568 mμ) was plotted against volume of the titrant added, with corrections being made for dilution, of course. The curvature is primarily due to the incompleteness of the reaction between zinc and XO under the experimental conditions. An additional cause of curvature is the overlapping formation of two different zinc-XO species, Zn(XO) and $Zn(XO)_2$, the stability constants of which do not differ greatly. There was no significant improvement when runs were made in media rich in ethanol or rich in dimethylsulfoxide.

2.2. Investigations Using PAR

The investigation was expanded using another titrant, namely PAR, which forms intensely colored complexes with zinc and other metals. A pH region exists wherein the red cadmium-PAR complex is destroyed by a high concentration of iodide while the red zinc-PAR complex is not destroyed. In addition, the restriction previously encountered of working at a pH of not more than 5.5 is no longer necessary since PAR, unlike XO, shows no pronounced color change due to changes in hydrogen ion activity even up to pH 8. Photometric titrations of zinc with PAR were attempted in the absence of both cadmium and iodide, and in the presence of iodide but not of cadmium. The pH region from 4 to 7 was studied using acetate and phthalate buffers to maintain the pH. Titrations were also made at pH 7 in an ammonium acetate medium and at pH 8 in a sodium acetate medium. In all cases the titration plots (absorbance at 508 mμ *vs* volume of titrant added) showed considerable curvature. Straight line regions and end points could only be guessed at and such end points lacked not only precision but also any reasonable relationship to the expected stoichiometry of the reaction. Here, as in the XO titration, curvature is due to the low stability of the zinc-titrant species and the simultaneous formation of the 1:1 and the 1:2 zinc-titrant complexes.

3. Extractive Photometric Determination of Zinc Using PAN

The failure for similar reasons of two different metallochromic indicators to serve as satisfactory photometric titrants for zinc suggested that future efforts should be directed toward the development of a photometric determination.

3.1. Introduction

The previously described properties of PAR which suggest it as a photometric titrant for zinc in cadmium also point towards its use as a photometric reagent for that metal. When such a use of PAR was attempted, it was observed that aqueous zinc-PAR solutions containing excess free PAR change color with time. The color change is from red to yellow to brown, the initial color depending on the ratio of complexed for free PAR. Below certain threshold concentrations of PAR, or zinc-PAR, or both, the color is stable for at least several days. Above the threshold concentrations, the rate of color change is proportional to the concentrations of PAR species, and, at a pH near 7, particularly to the concentration of free PAR. The addition of a limited amount of ethanol increases the time period of color stability; 20 to 40 per cent ethanol by volume is the optimum range. To a first approximation, ionic strength does not affect the color stability when the PAR or zinc-PAR is below the threshold concentration. No study of ionic strength effects was made above the threshold concentrations of these species. In all cases in which the color change was great enough to be visually apparent, the solutions gave a Tyndall effect. It appears that the zinc-PAR complexes are of low solubility in aqueous media and that slowly colloidal aggregates form; under certain pH and other conditions free PAR behaves similarly. Since the excess of free PAR required in a photometric zinc determination is sufficient to adversely affect the color stability of the solutions further investigations along this line were discontinued.

Attention was then directed to PAN, a dye that is similar to PAR in composition and in many of its properties. Cheng and Bray *(7)* report-

ed that PAN forms complexes with zinc, cadmium and many other metals. These complexes are insoluble in aqueous media and can be extracted into organic solvents readily. Of particular significance is the further finding by Shibata *(8)* that zinc is completely extracted in the form of its panates at a pH as low as 6 while cadmium panates are negligibly extracted under these conditions. The differences in the degree of reaction of zinc and cadmium with PAN attributable to pH masking are greater than with either XO or PAR. These differences can be enhanced by iodide masking of cadmium thus creating favorable conditions for an extractive photometric determination of small amounts of zinc in the presence of large quantities of cadmium.

3.2. Experimental

All work done in the development of an extractive photometric determination of zinc in cadmium was performed in a room in which the temperature was maintained reasonably close to 25°C by heating or air conditioning. The equipment and chemicals noted below were used.

Equipment

All spectral curves were made with a Bausch and Lomb 505 recording spectrophotometer. Absorbance measurements were made with that instrument in the maleate buffer work and with a Bausch and Lomb Spectronic 20 spectrophotometer in the phosphate buffer work. Beckman Zeromatic II pH meters were used for all pH measurements. The meters were standardized with buffer solutions prepared from Beckman powders. Good practice was followed in restricting the vessels used for the preparation and storage of solutions to borosilicate glassware or plasticware whenever appropriate. Class A volumetric glassware was used throughout without further calibra-

tion. Separatory funnels equipped with teflon stopcocks were used exclusively.

Chemicals

Water. Doubly deionized water was used exclusively.

Zinc Nitrate. A zinc nitrate stock solution was prepared from "Baker Analyzed" reagent zinc nitrate hexahydrate. The zinc concentration of the stock solution was determined to be 9.62×10^{-3} F by visual titration with a standard solution of EDTA in an ammonia-ammonium buffer of pH 10 using Eriochrome Black T as the indicator. By serial dilution solutions 9.62×10^{-4} F and 9.62×10^{-5} F in zinc were prepared. The standard EDTA solution was prepared by weighing a suitable quantity of primary standard grade disodium dihydrate of EDTA and making up to volume in a volumetric flask.

Cadmium Nitrate. "Baker Analyzed" reagent cadmium nitrate tetrahydrate, lot number 21252, was used to prepare solutions, 0.1, 1 and 4 F in cadmium. The zinc concentration of this cadmium salt was kindly furnished by the J. T. Baker Chemical Company of Phillipsburg, New Jersey. Two runs using flame absorption spectrophotometry gave values of 5×10^{-5} and 1×10^{-4} weight per cent zinc.

Other Metal Salt Solutions. "Baker Analyzed" salts (nitrates or chlorides) were used in the preparation of other metal salt solutions. Nitric or hydrochloric acid were added as necessary to dissolve the salts.

Chloroform. Fisher chloroform, N.F. was used throughout. The chloroform was washed with dilute aqueous hydrochloric acid to remove cations prior to use. A little ethanol which serves as a stabilizer was

added to the chloroform after the washing.

Alcohol. U. S. Industrial Chemical Company 95 per cent ethanol was used throughout.

PAN. Fisher Certified PAN was used to prepare a stock 1×10^{-2} F ethanolic solution. A 0.62 gram portion of PAN was dissolved in and brought to 250 ml with ethanol.

Maleic Acid and Maleic Acid-Maleate Buffer. Eastman technical grade and Matheson, Coleman and Bell maleic acid were used to prepare buffers. An approximately 1 F maleic acid solution was prepared by weighing out the solid. The room temperature pH of the solution was raised to about 7 by the addition of 50 per cent aqueous sodium hydroxide. It was necessary to extract the solution with dithizone in chloroform to remove impurities. After the extraction, the solution was diluted to about 0.5 F and the pH adjusted to 6.8 with hydrochloric acid and/or sodium hydroxide. The buffer was useable for only a few days or weeks after its preparation depending on the experimental conditions of its use, the condition of the laboratory atmosphere, etc. Attempts to extend the useful life of the buffer by adding thymol as a bactericide were unsuccessful. The effectiveness of mercuric iodide as a preservative could not be evaluated as the presence of mercuric ion in the backwash solution prepared from this buffer ultimately interfered in the finish of the zinc determination. A description of the problems associated with the use of a buffer that was not fresh, and a partial solution of these problems is presented in section 3.6.

Phosphate Buffer. The buffer was prepared by mixing 0.08 F phosphoric acid and 0.08 F potassium phosphate in quantities such that the

solution, after cooling to room temperature, gave a meter reading of pH 7.2. This solution was then extracted with dithizone in chloroform. Fisher reagent phosphoric acid and "Baker Analyzed" potassium phosphate were used to prepare the original 0.08 F solutions.

Sodium Hydroxide. "Baker Analyzed" reagent 50 per cent aqueous sodium hydroxide was used.

Potassium Iodide. "Baker Analyzed" reagent, Baker U.S.P. and Curtin U.S.P. grade potassium iodide were used interchangeably. No differences were discernable.

Potassium Cyanide. "Baker Analyzed" reagent potassium cyanide was used to prepare a 1 F solution. More dilute solutions in decade steps were prepared by serial dilution.

Sodium Thiosulfate. "Baker Analyzed" reagent sodium thiosulfate pentahydrate was used to prepare 1 F solution in freshly boiled water. The solution was stabilized with a small quantity of sodium carbonate.

Tartrate solution of pH 6.8. "Baker Analyzed" reagent d-tartaric acid was used to prepare 1 F solution. Sodium hydroxide was added to adjust the pH to 6.8.

Ascorbic Acid. Eastman l-ascorbic acid was used.

Acids and Ammonia. Fisher reagent concentrated acids and ammonia were used.

Other Reagents. "Baker Analyzed" reagents were used except as noted above.

3.3 Preliminary Investigations

A systematic investigation was begun of the behavior of solutions containing zinc, cadmium and PAN.

From a medium buffered at pH 5.5 with acetic acid-acetate, it was found that the zinc is partially extracted into chloroform as a panate. However, even in the absence of cadmium and iodide and using only a minimal amount of the buffer, two or three complete cycles of PAN addition and chloroform extraction are required for the quantitative recovery of zinc. While no cadmium is extracted under these conditions, a number of the impurities likely to be found in "pure" cadmium also form extractable red panates which interfere with a zinc determination. The addition of a little iodide could mask some of the interferences, notably copper and lead, at the expense of increasing the number of extraction cycles required to obtain the zinc, while an increase in the pH should improve the efficiency of the zinc extraction but seriously affect the selectivity in the presence of a large excess of cadmium. However, the combination of a moderate increase in pH and a massive addition of iodide was expected to provide optimum conditions for selectivity and extraction efficiency. Since the buffer capacity of an acetic acid-acetate buffer is inadequate at a pH greater than 5.7 it became necessary to select a different and suitable buffer. A phosphate buffer is usually used to maintain a pH in the vicinity of 7. However there was a reasonable possibility that the introduction of phosphate into the zinc-cadmium system would result in undesirable extraneous phenomena such as precipitation or complexation. The use of phosphate buffer was deemed unwise at this early stage of the investigation and was deferred until such time as the system was better understood. A more innocuous means of maintaining the pH in the appropriate region was sought. An ammonium acetate medium was investigated. While it served as a barely adequate holding buffer at a pH around 7, its

capacity was so low that it was not possible to systematically vary the pH in that region and study the effect of pH changes on the properties of interest. Ultimately a maleic acid-maleate buffer was settled upon. At the concentration levels employed it serves primarily as a holding buffer, but has sufficient buffer capacity to allow a study of the effect of pH variations within the range 6.0 to 7.2.

Next, the formation of zinc panates in an aqueous iodide medium was investigated in solutions containing zinc alone as well as in solutions containing both zinc and cadmium. The following reactions are involved.

$$M^{2+} + \underline{x}I^{-} = MI_x^{+(2-x)} \qquad (I)$$

$$M + \underline{y}(PAN)_{(aq)} = M(PAN)_{y(s)} \qquad (II)$$

$$PAN_{(aq)} = PAN_{(s)} \qquad (III)$$

where M is zinc or cadmium, $\underline{x}$ is 1, 2, 3 or 4 and $\underline{y}$ is 1 or 2. Charges are not essential and are omitted for simplicity in Equation (II).

As a PAN solution in alcohol is added to the aqueous medium containing zinc (but no cadmium) some of the metal is complexed and precipitated according to Equation (II). Simultaneously, localized high concentrations of PAN occur and the water-insoluble PAN precipitates (Equation III). The reactions proceed far to the right due to formation of sparingly soluble substances. Less than one minute after its addition the concentration of free dissolved PAN has been so diminished by precipitation of PAN species that the rate of formation of zinc panates becomes too low to be of analytical value although excess PAN remains in the system.

From the foregoing it follows that the mode of PAN addition is

critical. Procedural variations that avoid the precipitation of free PAN were tried but found to be of no value. When PAN is used in the form of a solution in chloroform rather than in ethanol no visible quantity of red zinc panates are formed even upon shaking the system containing the two liquid phases for many minutes. This observation is not surprising. It is generally accepted *(9)* that in two-phase systems such as the one just described the extractable species forms in the aqueous phase and not at the interface or in the organic phase. The extraction of the preformed complex is rapid and its formation is the rate determining step. Since the solubility of PAN in chloroform is so much greater than its solubility in water the concentration of PAN in the aqueous phase is extremely low. Consequently, the rate of formation of zinc panates in the two-phase system is exceedingly slow. While zinc panates are formed without difficulty if PAN is added to a medium sufficiently rich in ethanol to present the precipitation of free dye, the use of such a procedure will have serious adverse consequences when a selective method for determining zinc in the presence of excess cadmium is sought. This will be elaborated upon shortly. A satisfactorily complete chelation of the zinc by the PAN is obtained by incremental addition of the required amount of PAN in the form of an ethanolic solution of suitable concentration shaking briefly after having added each increment.

The criticalness of the mode of addition of PAN is emphasized by the finding that more PAN is required to effect the complete reaction of zinc when the PAN is added as a 0.025 F ethanolic solution rather than as a 0.01 F ethanolic solution. This observation may be explained in terms

of the greater local concentrations of free PAN and the consequent more rapid precipitation of that species when it is added in the form of a somewhat more concentration solution.

Attention was then directed to a system containing both zinc and cadmium. Here the two metals compete for the limited amount of PAN added and the bulk of the PAN is acquired by the metal present in excess.

The precipitation of the highly insoluble zinc panates, cadmium panates and free PAN is reasonably rapid but the exchange reactions involving the precipitated species are exceedingly slow. Thus even after several minutes the quantities of zinc panates and cadmium panates which are present differ but little from the amounts of these species initially formed, i.e., formed during the short time within which a significant amount of dissolved PAN was available. Since the system under investigation contains a great excess of cadmium that species must be masked in order for the acquisition of PAN by zinc to be statistically favored, and the masking must be selective. The formation constants of the iodide complexes of cadmium are several orders of magnitude greater than those of zinc *(10)*. Thus, the presence of a high concentration of iodide in the aqueous medium allows the zinc to compete successfully for the added PAN despite the large excess of cadmium.

It was observed that extended agitation of the aqueous system containing zinc, cadmium, iodide and PAN leads to a decrease in the quantity of zinc panates found in the organic layer after extraction. It had been expected that more zinc panates would form at the expense of cadmium panates if the system were given sufficient time to equilibrate as the zinc panates are the more stable panates. (The greater stability of the zinc

panates is indicated by the previously mentioned report *(8)* that these panates can be formed and extracted at a lower pH than cadmium panates.) The discrepancy between the expected and the experimental findings may be due to the failure to take into account the effect of the differing insolubilities of the various species upon the competing equilibria shown in Equations II and III. If cadmium panates are less soluble in water than zinc panates then, regardless of their relative stabilities, extended shaking prior to the addition of the organic phase will result in a reduction in the amount of zinc panates found in the extract. If free PAN is less water soluble than zinc panates the consequences of extended shaking will be similar. Unfortunately pertinent solubility data is lacking.

Whatever the causes of incomplete formation of zinc panates, experiments showed that the best results are obtained if the system is s shaken for an intermediate period of time. As long as any appreciable quantity of free PAN is present in the aqueous medium, shaking will increase the quantity of zinc ultimately present as panates; but continuing to shake after the free PAN has essentially fully precipitated will reduce the amount of zinc panates eventually available for extraction. In this system attaining the desired analytical result is dependent upon taking advantage of the kinetics of some of the various reactions and not upon achieving equilibrium in all cases.

The addition of PAN to a hot solution containing zinc, cadmium and iodide was investigated. Under such conditions there would be an increase in the rates of the various exchange reactions and it might be possible to approach or even attain equilibrium for the exchange reactions. Since the values of the temperature coefficients for the pertinent stability

constants and solubilities were not known there was the possibility that attainment of such an equilibrium state would favor the complete formation of zinc panates. Experimentally it was found that the addition of PAN to the hot solution results in a decrease in the quantity of zinc panates recovered upon extraction. From observations made in the course of the addition of PAN it appears that at higher temperatures the iodide fails to mask cadmium to as great an extent as at room temperature. Hence the cadmium is statistically favored in the competition for added PAN. The favorable consequences, if any, of allowing the system to approach or reach equilibrium do not compensate for the adverse effects of the high temperature upon the stability of cadmium iodide complexes.

After discovering a means of achieving a complete conversion of zinc to its panates, even in the presence of cadmium, attention was directed towards the attainment of selectivity. The selective separation of zinc panates from cadmium is primarily dependent on the choice of a suitable organic solvent for the extraction. The critical property seems to be the solubility of water in the organic material. Three solvents were investigated: chloroform, amyl alcohol and ethyl acetate. Water is the least soluble in chloroform and a chloroform extraction gives by far the best separation. With each solvent the metal panates and all the free PAN are extracted almost instantaneously. With chloroform, but not with the other two solvents, this phenomenon is rapidly followed by the backtransfer of almost all the cadmium to the aqueous layer if that layer has a suitable pH and iodide concentration. The investigations using amyl alcohol and ethyl acetate as extractants were abandoned since the selectivity achieved with these solvents is worse by several orders of

magnitude than that attained with chloroform. When utilizing chloroform under suitable operating conditions it is possible to obtain a cadmium to zinc ratio in the extract of about 1:1, whereas the original ratio in the aqueous solution was considerably greater than 10,000:1. It may well be that the failure to obtain a complete separation in a single chloroform extraction is attributable to the slight amount of water incorporated into the chloroform phase. It should be noted that the small amount of alcohol introduced as a result of the requirement that PAN be added as an ethanolic solution increases the solubility of water in chloroform.

The extractive separation of zinc and cadmium depends on the kinetics of backtransfer as well as on the use of a suitable solvent. The equation for the backtransfer reaction may be written as

$$M(PAN)_{y(CHCl_3)} + \underline{x}I^- = MI_{x(aq)}^{+2-x} + \underline{y}PAN_{(CHCl_3)} \qquad (IV)$$

where M, $\underline{x}$ and $\underline{y}$ are defined as in Equations I-III. In the case of cadmium the equilibrium lies far to the right and the reaction is rather fast. With zinc the reaction goes quite slowly and equilibrium is not attained within the time periods which were investigated. Fortunately there is no need to determine how far to the right the reaction will go at equilibrium. It suffices to know that only upon prolonged shaking or even lengthier contact between the two phases without agitation is there a backtransfer of any zinc. The use of a shaking time of intermediate duration, about twenty seconds, takes advantage of the difference in the rates of backtransfer of cadmium and zinc and results in a good separation as well as in the complete retention of the preformed zinc panates

in the organic layer. In an entirely different metal-PAN system, namely In-PAN, Zolotov and coworkers *(11)* observed a similar backtransfer phenomenon. These authors found that preformed In-PAN was completely and rapidly extracted into chloroform. However, if shaking was continued the amount of In-PAN in the organic layer decreased with time until the equilibrium value was reached. From the other direction, that is, extracting an indium-containing aqueous phase with a chloroform solution of PAN, equilibrium was also attained, of course, but only after more than an hour of shaking.

The rapid and complete backtransfer of cadmium may be due to its ability to change its structure to a six-coordinate species from the four-coordinate monomeric species assumed to be originally extracted. The considerable stability of cadmium iodide complexes aids this change. During shaking the two positions of the six coordinate species which are not occupied by PAN may acquire water or, more likely, iodide. The resulting species will not return to the organic phase, either due to its hydration or its charge. The labile PAN will then extract. The probability of zinc being backtransferred is far less. Zinc is smaller and will have a lesser tendency to increase its coordination number from four to six. Zinc also forms far weaker iodide complexes than cadmium so the iodide will not aid in the expansion of the coordination sphere as much as it does in the case of cadmium.

It was found that, at least over the pH range 7.0-7.4, no zinc is backwashed into a saturated aqueous potassium iodide medium within a reasonable time from a chloroform medium containing zinc panates. Cadmium is rapdily and quantitatively backwashed upon shaking for a short time.

The data obtained in the backwashing experiments with respect to pH and iodide concentration have obvious implications as to the optimal conditions for the original formation of the zinc panates and their extraction.

Betteridge, Fernando and Freiser *(12)* reported that zinc forms two panates, Zn(PAN) and $Zn(PAN)_2$. The equation representing the equilibrium between these species and free PAN is shown below. The number beneath each species is the wavelength of its absorbance maximum in a chloroform solution.

$$\underset{556\ m\mu}{Zn(PAN)_2} = \underset{517\ m\mu}{Zn(PAN)} = \underset{495\ m\mu}{PAN} \qquad (V)$$

Since there are only two zinc panates it is possible to make the zinc determination by operating at the isosbestic point. This is not done as a considerably greater sensitivity is obtained by making measurements at the wavelength of the absorbance maximum of one of the zinc species. This approach, of course, requires the conversion of all the zinc to the selected panate. In the zinc-PAN system it is necessary to work with zinc $(PAN)_2$ for the following reasons. Firstly any analytical use of absorbance measurements at 517 mμ (the absorbance maximum of the 1:1 complex) is precluded by the large absorptivity on free PAN at this wavelength. Secondly, there is no PAN to zinc ratio that yields the 1:1 complex as the sole zinc-containing species. If the PAN:Zn ratio is small non-chelated zinc will be present along with the 1:1 complex while if the ratio is large at least some of the 1:2 complex will form. To convert all the zinc to $Zn(PAN)_2$ requires an excess of PAN. Within the zinc concentration range (up to about 1.1 μg/ml) that yields useful absorbance

values (up to about 0.9) at 556 mμ in a 1-cm cell it was found that an 8:1 PAN to zinc molar ratio was necessary and sufficient to convert essentially all the zinc to the 1:2 complex. This follows from the observation of an absorbance peak at 517 mμ which appears whenever the PAN to zinc molar ratio is less than 8:1. Since free PAN has a small but finite absorptivity at 556 mμ and its presence in sizable excess is necessary its contribution to the measured absorbance at 556 mμ must be considered in the zinc determination. Either a correction must be applied or, more practically, the approach of operating with the same fixed total quantity of PAN in both calibration and analysis must be employed. Obviously if the latter procedure is selected the fixed amount of PAN to be added must be, on a molar basis, eight times the largest amount of zinc expected to be encountered. With the high molar absorptivity of the $Zn(PAN)_2$ species, the quantity of zinc permissible is, of course, limited. Actually, the use of an 8:1 molar ratio contains a built-in safety factor since the absorbance at 556 mμ of a zinc panate system reaches its constant and maximum value, within experimental errors, at molar ratios of only 4:1. This observation can be explained as follows. While the peak due to the 1:1 complex does not completely disappear at this PAN to zinc molar ratio it becomes very small. Hence, almost all the zinc is present as $Zn(PAN)_2$ even if on a molar basis PAN:Zn = 4:1. Furthermore, the absorptivity of the 1:1 complex is considerable at 556 mμ.

Perfect phase separation is difficult or impossible to attain and when the organic layer is drained after an extraction or backwashing a small turbidity usually is found in the extract. This turbidity is removed by addition of some alcohol. It was found that if a chloroform

solution of zinc panate having a molar PAN to zinc ratio of at least 8:1 is diluted with as much as 30 per cent alcohol by volume, the change in the absorbance at 556 mμ is linearly proportional to the dilution. For example, dilution of 40 ml of the chloroform solution to 50 ml with ethanol changes the absorbance to four-fifths of its initial value. It is reasonable to conclude that the addition of the limited amounts of alcohol specified above does not significantly change the position of the equilibrium of Equation V and that the value of the absorptivity of $Zn(PAN)_2$ is the same in chloroform-alcohol as it is in chloroform. The addition of alcohol has no influence on the stability of the color. With or without alcohol the color is stable within the precision of the instrument for at least 24 hours.

$Zinc(PAN)_2$ in chloroform-ethanol obeys Beer's Law at least up to a concentration of 1 μg of zinc per ml of solution. The absorbance at 556 mμ of a 50 μg portion of zinc in a 50 ml extract is found to be about 0.88 in a 1-cm cell. Thus the molar absorptivity is found to be 5.8×10^4 liters/mole cm and is in satisfactory agreement with Püchsel's value, 5.55×10^4 *(13)*, but both of these values differ considerably from that reported by Shibata *(8)*.

Chloroform dissolves traces of stopcock grease. The grease dissolved in the zinc-PAN extract causes the initially observed absorbance at 556 mμ to be less than that expected and the absorbance continued to decrease with time for periods in excess of 24 hours. Thus the use of a glass plug separatory funnel is undesirable. Prolonged contact of the organic phase with an aqueous phase, e.g., failure to separate the layers promptly after extraction, as noted above, also results in an absorbance

at 556 mμ lower than that expected; however, the color stability of the separated layer is not affected.

Attempts were made at masking cadmium with varying sub-stoichiometric quantities of EGTA using the approach of Flaschka and Garrett *(14, 15)*, rather than with iodide. In all cases the results for zinc were drastically lower than expected due to the failure of EGTA to complex the cadmium with sufficient selectivity. Depending on the quantity of EGTA taken, either the cadmium is insufficiently masked with respect to PAN or the zinc is partially masked.

3.4. Procedures (Maleate Buffer)

Using the information acquired in the preliminary investigations and in the course of the interference studies, procedures were devised for the determination of zinc in cadmium.

The procedures which follow are suitable for application to cadmium or cadmium salt samples having a cadmium to zinc molar ratio not exceeding 100,000:1 or a weight ratio not exceeding 170,000:1. Furthermore the cadmium content of the samples must not exceed about 50 μg. Samples having a larger cadmium to zinc ratio than specified above may be treated by the procedures described in section 3.7.

A thorough consideration of the ruggedness of the procedures appear in Section 3.6. Considering the results of the ruggedness test it can be stated that the values specified for quantities of reagents to be added and for shaking times are intended merely to serve as guides. The sole exception to the preceding statement is that the quantity of potassium cyanide called for in step 4 must not be exceeded. Furthermore, if the volume of the system exceeds about 30 ml prior to the addition of the

buffer in step 4, the amount of buffer to be taken should be increased proportionately.

Basic Procedure

The basic procedure is capable of handling samples containing a number of extraneous cations. The tolerance limits for these cations can be found in Table 10.

Step 1. Place the sample in a volumetric flask and dissolve in the minimum amount of water, or if necessary, hydrochloric or nitric acid. Bring to volume with water. Transfer an aliquot of suitable size to a 50 ml beaker (Note 1).

Step 2. Add 1 ml of tartrate solution of pH 6.8, 20 g of potassium iodide (Note 2) and sufficient water to dissolve all solids (Note 3).

Step 3. Immerse the electrodes of a pH meter in the solution and add sodium hydroxide and hydrochloric or nitric acid as necessary until a meter reading of about 7 is obtained.

Step 4. Add 2 ml of 1 F sodium thiosulfate and a spatula tip of ascorbic acid (Note 4). Add 1 drop of 1 F potassium cyanide. Add 5 ml of maleic acid-maleate buffer (Note 5). Now proceed without undue delay.

Step 5. Transfer the solution to a 60 or 125 ml separatory funnel equipped with a teflon stopcock.

Step 6. Add 0.7 ml of 1×10^{-2} F PAN in 95% ethanol in increments of 0.1, 0.1, 0.1, 0.1 and 0.3 ml. Shake for 2 to 5 seconds after adding each 0.1 ml increment and for 45 seconds after adding the final increment.

Step 7. Add 6 to 10 ml of chloroform and shake for 20 seconds. Add water to almost fill the separatory funnel (Note 6) and shake briefly. Allow the phases to separate.

Step 8. Drain the organic layer into a second separatory funnel, the stem and stopcock bore of which must be free of water.

Step 9. Extract the aqueous layer remaining in the first separatory funnel with five 3 to 4 ml portions of chloroform (Note 7). Collect all the extracts in the second separatory funnel.

Step 10. To the combined chloroform extracts add 10 ml of a previously prepared backwash solution (Note 8) and a spatula tip of ascorbic acid. Shake for 20 seconds. Add water to aid the separation of the layers and shake briefly. Allow the phases to separate.

Step 11. Drain the organic layer into a dry 50 ml volumetric flask. Wash the aqueous phase with two 3 to 4 ml portions of chloroform (Note 7). Collect all the organic phases in the volumetric flask.

Step 12. Add 10 ml of 95% ethanol to the volumetric flask and mix. Allow the system to warm to room temperature and then bring to volume with chloroform (Note 9).

Step 13. Measure the absorbance of the chloroform-ethanol solution in a 1-cm cell using water as the reference. Operate at the wavelength of the absorbance maximum (about 550 mμ) (Note 10).

Step 14. Determine the zinc content of the solution by referring to a calibration curve. The calibration curve is obtained by plotting absorbance vs quantity of zinc for a series of zinc standard solutions which contain no cadmium and have been treated as

described in Steps 1 to 13 above (Note 11).

Note 1. If the composition of the sample and its mode of dissolution are such that Step 3, neutralization, is unnecessary the solution may be transferred directly to the separatory funnel instead of the beaker.

Note 2. The 20 g quantity specified contains a reasonable safety factor even for samples having a cadmium content of 1 g. For samples having a cadmium content of less than 1 g it may be permissible to use less than 20 g of potassium iodide. No study was made of the ratio of potassium iodide to cadmium that was required. If the procedure is to be applied routinely and frequently, economics would make such an investigation worthwhile.

Note 3. There is some reason to believe that marginally better results are obtained if the solution cooled by the dissolving of the salt is not allowed to warm to ambient temperature before proceeding. There is certainly no reason to lengthen the time of the determination by allowing the solution to warm.

Note 4. The size the spatula that was employed was such that a spatula tip of ascorbic acid had a mass of between 2 and 4 mg.

Note 5. If the electrodes of a pH meter are immersed in the cold solution which is on hand at this point, the meter should read "pH" 7.1 to 7.3. The discrepancy between this value and the nominal pH value of the buffer, 6.8, stems from the grossly changed conditions (lower temperature and much greater ionic strength). Under these conditions reference is clearly and appropriately made to "meter reading" instead of pH value.

Note 6. In the absence of added water the two phases have approximately equal densities and the layers fail to separate.

Note 7. If the organic phase is colorless after use of less than the specified number of portions of chloroform it is not necessary to continue the treatment with that liquid. Instead, proceed to the next step.

Note 8. Prepare the backwash solution as follows: Place 50 g of potassium iodide, 18 ml of maleic acid-maleate buffer, 5 ml of tartrate solution of pH 6.8, 5 ml of 1 F sodium thiosulfate and water in a beaker that has volume markings. After dissolution is complete add water to bring the solution volume to 100 ml. The backwash solution is stable for weeks or months and may be prepared in advance in large lots.

Note 9. A negative error not exceeding 3 per cent occurs if the solution is made up to volume immediately without waiting for it to warm to ambient temperature.

Note 10. The precise wavelength of the absorbance maximum must be determined empirically for the instrument used. An instrumental parameter, namely the bandpass, is involved because the working solution contains not one but two species, $Zn(PAN)_2$ and free PAN, which absorb light in the wavelength region of interest. For routine work it is permissible to operate at the wavelength of the absorbance maximum of the species of interest, $Zn(PAN)_2$, which is 556 mμ.

Note 11. Short cuts and economies are permissible in obtaining the calibration curve. When working with the zinc standard solutions

it is permissible to use 10 g of potassium iodide rather than 20 g (Step 2) and to omit the backwash operation.

Simplified Procedure

The simplified procedure differs from the basic procedure only slightly, in that the species that are introduced in the basic procedure in order to mask extraneous cations are omitted from the simplified procedure. The species referred to are tartrate and thiosulfate.

To determine zinc in cadmium by means of the simplified procedure carry out Steps 1 through 14 of the basic procedure with the following exceptions:

Step 2. Omit the addition of tartrate solution of pH 6.8.

Step 4. Omit the addition of sodium thiosulfate.

Furthermore in preparing the backwash solution (Note 8) omit the addition of the tartrate solution of pH 6.8 and the sodium thiosulfate. It is perhaps too obvious to mention but in preparing the calibration curve for the simplified procedure, the zinc standard solutions should be treated by that procedure. The notes of the basic procedure are equally valid for the simplified procedure provided Note 8 is modified as indicated above.

3.5. Study of Samples Containing Only Zinc and Cadmium

A quantitative study was begun of solutions containing both zinc and cadmium but no other metals which react with PAN. The necessary solutions were prepared by mixing measured volumes of standard zinc and cadmium stock solutions in appropriate ratios. Pipets or burets were used to deliver the zinc solution and graduated cylinders were employed for the

cadmium solution. Since the stock solutions contained were not strongly acidic preneutralization was unnecessary.

3.5.1. Results and Discussion. Table 1 gives the results of a series of runs using the basic procedure. Table 2 gives the results of a series of runs using the simplified procedure.

With quantitative data now being available consideration was given to the crucial matter of the reliability of the procedures. In order to evaluate the accuracy of the results yielded by the use of the procedures it was necessary to know the amount of zinc taken so that a comparison could be made with the experimentally determined amount of zinc found. The quantity of zinc taken was the sum of two numbers; one representing the zinc content of the standard zinc stock solution and the other attributable to the zinc content of the standard cadmium stock solution since, as noted earlier, a zinc impurity always accompanies cadmium. Obtaining valid estimates of the zinc content of the cadmium solution was not simple. It was not permissible to avoid the problem entirely by assuming that the zinc content of the cadmium salt made a negligible contribution to the total quantity of zinc taken since, in the work presented here, the cadmium to zinc ratio was very large.

As a starting point calculations were made of the amount of zinc contained in portions of cadmium of the sizes used in this investigation, these calculations being based on value of the zinc content of the cadmium nitrate tetrahydrate that appeared on the label of the bottle, 0.001 per cent. The results of the calculation, which are shown below, clearly indicate that the zinc impurity in the cadmium salt should account for a significant or even, in some cases, a major fraction of the total zinc in the artificial samples.

Table 1. Results of the Determination of Zinc in Cadmium Using the Basic Procedure. (Each Line Presents the Data Obtained from a Single Run.)

Quantity of Cadmium Taken, µg	Quantity of Zinc Found, µg	Quantity of Zinc Taken, g: As Dilute Standard Zinc Nitrate Solution	Quantity of Zinc Taken, g: As an Impurity in the Cadmium	Error: µg	Error: %	Cadmium:Zinc Molar Ratio in Thousands
0.22	12.8	12.6	0.2	0	0	10
0.22	24.9	25.2	0.2	-0.5	-2	5
0.22	37.4	37.8	0.2	-0.6	-2	3.3
0.45	12.8	12.6	0.5	-0.3	-3	20
0.45	25.6	25.2	0.5	-0.1	0	10
0.45	37.7	37.8	0.5	-0.6	-2	5
0.45	50.1	50.4	0.5	-0.8	-2	2.5
0.90	4.2	3.2	1.0	0	0	120
0.90	7.1	6.3	1.0	-0.2	-3	70
0.90	12.8	12.6	1.0	-0.8	-6	40
0.90	26.3	25.2	1.0	+0.1	0	20
0.90	37.9	37.8	1.0	-0.9	-2	13
0.90	50.5	50.4	1.0	-0.9	-2	10

Table 2. Results of the Determination of Zinc in Cadmium Using the Simplified Procedure

Quantity of Cadmium Taken, g	Number of Runs	Quantity of Zinc Found Mean, µg	Quantity of Zinc Taken, µg		Error		Average Deviation of the Mean, µg	Cd:Zn Molar Ratio in Thousands
			As Dilute Standard Zinc Nitrate Solution	As an Impurity in the Cadmium	µg	%		
0.22	3	13.2	12.6	0.2	+0.4	+3	0.1	10
0.22	3	25.5	25.2	0.2	+0.1	0	0.5	5
0.45	4	13.2	12.6	0.5	+0.1	+1	0.4	20
0.45	3	25.9	25.2	0.5	+0.2	+1	0.1	10
0.45	4	50.6	50.4	0.5	-0.3	-1	1.2	5
0.67	2	12.8	12.6	0.7	-0.5	-4		30
0.67	1	25.9	25.2	0.7	0	0		15
0.67	3	38.2	37.8	0.7	-0.3	-1	0.4	10
0.90	3	13.9	12.6	1.0	+0.3	+2	0.2	40
0.90	3	26.0	25.2	1.0	-0.2	-1	0.3	20
0.90	2	50.5	50.4	1.0	-0.9	-2	0.8	10
1.34	1	14.2	12.6	1.5	+0.1	+1		50
1.34	1	38.7	37.8	1.5	-0.6	-2		20
1.8[1]	1	51.1	50.4	2.0	-1.3	-3		20
2.7[1]	1	26.2	25.2	3.0	-2.0	-8		50
2.7[1]	1	39.3	37.8	3.0	-1.5	-4		40
3.6[1]	1	51.6	50.4	4.0	-2.8	-6		40

[1]The quantity of potassium iodide added (Step 2) was increased to 13 g of KI per g of cadmium. Furthermore, as more than the normal volume of water then had to be added (Step 2) in order to dissolve all the solids, the volume of maleate buffer added (Step 4) was increased proportionately.

Quantity of Cadmium, g	Zinc content, µg
0.22	6.2
0.45	12.3
0.67	18.5
0.90	24.6
1.34	36.9
1.8	49
2.7	74
3.6	99

However, as is shown in Tables 1 and 2, there is almost perfect agreement between the quantity of zinc taken in the form of a dilute standard zinc nitrate solution alone and the total quantity of zinc found. Had the 0.001 per cent figure been even approximately correct such agreement would have required that the per cent of zinc recovered vary from as little as 25 per cent in some runs to as much as 100 per cent in other runs with a number of values in between. Furthermore this variation would have had no obvious correlation with the quantity of zinc taken, the quantity of cadmium taken or the cadmium to zinc ratio. Some explanation of the observed agreement other than remarkable coincidence was sought.

From the data obtained it was obvious that the commonly used method of standard additions would be of no value in this case. The zinc content of any reasonable size increment of cadmium was so small as to be, at most, comparable to the sensitivity limit of the procedure. Only be taking large increments of cadmium would it be possible to add enough zinc to significantly exceed the sensitivity limit. However preliminary ex-

periments had shown that if a large quantity of cadmium were taken there would be a decrease in the per cent of the total zinc which was recovered as panates in the chloroform extract. It appeared that cadmium in large amounts interfered with the formation of zinc panates or their extraction or both.

An alternative was to adopt a value for the zinc content that leads to reasonable agreement between the quantity of zinc taken and the quantity of zinc found. Since it was evident that there were negative errors in the amount of zinc found whenever the cadmium content of a run exceeded 1.34 g such runs were not considered in determining the adopted value. Using the data obtained in the runs listed in Tables 1, 2 and 4, the value that led to best agreement was 4×10^{-5} per cent. While this procedure of necessity leads to internal consistency there is ample reason to question whether the results so obtained are valid. Fortunately at a later date it was possible to analyze the cadmium salt for its zinc content by an entirely independent method, namely by flame absorption photometry. Two runs yielded values of 1×10^{-4} and 5×10^{-5} per cent respectively. The low precision of the atomic absorption data is attributable to the need to use a great quantity of cadmium salt in order to obtain a sufficiently large signal for the zinc. Thus the solution used had a high solute concentration and rapidly clogged the burner. Measurements had to be made very quickly and such conditions are not conductive to results of high precision. Under these circumstances, the agreement between the adopted value, 4×10^{-5} per cent, and the atomic absorption values is satisfactory.

Shown below is the amount of zinc in μg contained in various quan-

tities of cadmium at various values for the per cent of zinc in the cadmium salt.

	Percent Zinc in the Cadmium Salt				
	2×10^{-5}	4×10^{-5}	6×10^{-5}	8×10^{-5}	1×10^{-4}
Quantity of Cadmium, g	Zinc in µg				
0.22	0.1	0.2	0.4	0.5	0.6
0.45	0.2	0.5	0.7	1.0	1.2
0.67	0.4	0.7	1.1	1.5	1.8
0.90	0.5	1.0	1.5	2.0	2.5
1.34	0.7	1.5	2.2	3.0	3.7

From the above, and bearing in mind that the results of the procedure are good to only about ±0.5 µg, it can readily be seen why the method of standard additions is inapplicable in this case in determining the zinc content of the cadmium salt. Furthermore, if the above numerical values are used in conjunction with the data of Tables 1 and 2 it can be calculated that the per cent error in the quantity of zinc found is in most cases not significantly senstivite to the uncertainty in the zinc content of the cadmium. Only in samples containing very little zinc or a great amount of cadmium or some combination of these factors will the uncertainty associated with the zinc content of the cadmium salt significantly affect the error.

Having resolved the question of the zinc content of the cadmium salt attention was now directed towards error analysis.

Table 2 shows that a large negative error occurs whenever a sample

contains considerably more than 1 g of cadmium. A reasonable explanation is that the added potassium iodide, even if present in the weight ratio of 13:1 with respect to cadmium, fails to mask the cadmium completely against reaction with PAN. Much of the PAN added to the aqueous phase is thus bound to cadmium and then, being kinetically blocked, is unable to react with the zinc. Consequently, only a fraction of the zinc originally present ends up in the extract. Neither doubling the quantity of PAN added nor increasing the ratio of potassium iodide to cadmium to 20:1 by weight gives a significant improvement. Although the zinc losses are much smaller in samples having a lower cadmium content it is obvious from the data presented in Tables 1 and 2 that there is a systematic negative error inherent in the zinc determination. Thus the phenomenon described above appears to be the principal source of error.

Since the increase in negative errors is less than proportional to the increase in zinc content, samples containing much zinc usually show the greatest absolute errors and the smallest percent errors. Conversely samples containing the smallest amounts of zinc tend to have the lowest absolute errors and the largest percent errors. It also follows that for samples containing less than 1 g of cadmium the percent error is primarily dependent on the amount of zinc present and not on the cadmium to zinc ratio.

It may appear that the results shown in Table 2 which are derived from the application of the simplified procedure are of somewhat better quality than the results listed in Table 1 which have been obtained by use of the basic procedure, however this is not the case. It should be noted that the data in Table 2 are, in most cases, mean values of the re-

sults of several runs while Table 1 presents the results of single runs exclusively. The standard deviation of the absolute error for all the individual runs represented in Table 2 except the last four is 0.7 µg while the same quantity for Table 1 is 0.6 µg. Since systematic errors as well as random errors contribute to the standard deviations above, and since the two sets of data are not matched in terms of the distribution of zinc contents and cadmium contents, the standard deviations are not strictly comparable. However they do strongly indicate that, when applied to systems containing only zinc and cadmium, the basic procedure and the simplified procedure yield equally good results.

3.6. Study of the Ruggedness of the Procedure

A systematic study was made of the ruggedness of the basic procedure using the eight combinations of seven factors method of Yooden *(16)*. The eight runs were made using sample portions containing 26.2 µg of zinc and either 0.22 or 0.45 g of cadmium hence the cadmium to zinc molar ratio was either 5,000 or 10,000 to 1. Since the item of interest was reproducability rather than the value of the zinc content of the sample no calibration curve was prepared and the results are presented as absorbance values rather than as µg of zinc. The consistency of the results in terms of a quantity of zinc may be readily calculated from the fact that 0.010 absorbance units corresponds to 0.60 µg of zinc. The results are shown in Table 3. It can be seen that all of the changes made in the listed variables had essentially no effect on the results.

Other observations indicated that the results were not affected by any of the following variations:

1. Adding a quantity of PAN between 0.6 and 0.8 ml (Step 6).
2. A deviation of ± 20 per cent in the size of each PAN increment (Step 6).

Table 3. Results of a Ruggedness Test

Run Number	1	2	3	4	5	6	7	8
Ml of 1 F Cd Stock Solution	2	2	2	2	4	4	4	4
Ml of Solution Containing 1 F Sodium Thiosulfate and Tartrate Solution of pH 6.8 in a 2:1 Ratio	2	2	4	4	2	2	4	4
Dr of 1 F Potassium Cyanide	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5
Ml Aqueous Layer Before KI and Maleate Buffer Are Added	20	20	40	40	40	40	20	20
Grams of KI	10	20	10	20	20	10	20	10
Ml Maleate Buffer	4	8	8	4	4	8	8	4
Ml 95% Ethanol Added to Extract	9	13	13	9	13	9	9	13
Absorbance at 556 mμ	0.458	0.462	0.446	0.443	0.454	0.450	0.457	0.451

Absorbance, Mean of 8 Runs: 0.453 Standard Deviation: 0.006

Variable	Variation	Corresponding Absorbance
Volume of Cadmium Stock Solution	2 ml and 4 ml	0.452 and 0.453
Volume of TST Mixture	2 ml and 4 ml	0.456 and 0.449
Volume of 1 F KCN	0.25 dr and 0.5 dr	0.454 and 0.452
Volume of Aqueous Solution without KI and Buffer	20 ml and 40 ml	0.457 and 0.448
Mass of KI	10 g and 20 g	0.451 and 0.454
Volume of Buffer	4 ml and 8 ml	0.452 and 0.454
Volume of Ethanol	9 ml and 13 ml	0.452 and 0.453

3. A shaking time of from 30 seconds to 2 minutes after adding the final increment of PAN (Step 6).
4. A shaking time of from 15 to 35 seconds (Steps 7 and 10).
5. A backwash solution volume of from 8 to 20 ml (Step 10).

Although the method was quite insensitive to variations in the quantity of the various reagents used it was found to be very sensitive to the quality of the maleate buffer. If that buffer is not fresh, low and markedly erratic values are obtained for the zinc. Whenever this behavior occurred it was observed that some insoluble material accumulated at the water-chloroform interface during the extraction. The greater the quantity of this material, the more erratic the results. This material, which could not be identified, appeared in various forms and colors: wispy, gelatinous, almost colorless, whitish or redish. Among the factors affecting the amount of this material are the concentration of cadmium or iodide or both, and the age of the buffer. The material interferes with the analysis by absorbing zinc, PAN and zinc panates. It also greatly and adversely affects the degree of completeness attained in the separation of the layers. The interfacial material has a pronounced honeycomb structure which traps water and chloroform in its cells. The extent of the honeycomb formation is related to the interval between the addition of the buffer and the extraction of the panates; this is the major reason for proceeding with the analysis as quickly as possible after adding the buffer. This material is never produced in the backwashing operation and extraction. During the course of the anion interference study it was observed that the addition of cyanide suppresses the formation of the interfacial material to a considerable degree.

In the absence of cyanide, rapid work and the use of freshly prepared maleate buffer solution are needed to minimize the formation of this material and lessen the related detrimental effects on the zinc determination. If cyanide is added considerably older buffer solutions may be used and rapid work is no longer vital. Hence the addition of cyanide is desirable even when its presence is not required for masking purposes.

3.7. Methods Applicable to Samples Having Cadmium to Zinc Molar Ratios Exceeding 100,000:1

There is an inherent upper limit imposed on the cadmium to zinc molar ratio that can be handled by either the basic or the simplified procedure. Two factors account for this limitation. Firstly, as mentioned above, the procedures yield good results only if the size of the sample is such that its cadmium content does not greatly exceed 1 g. Secondly, there is a lower limit to the amount of zinc that must be present in the sample. This limit cannot be numerically specified but rather is governed by the relative accuracy and precision desired in the results, since, as is shown in Tables 1 and 2, the sensitivity of the method is about half a microgram. If one accepts a lower limit for the zinc content of 5 μg or, in other terms, accepts a relative error of about 10 per cent the procedure is applicable, without any modifications, to samples having a cadmium to zinc molar ratio up to about 100,000:1.

The development of a procedural variation that would extend the applicability of the method to samples having a larger ratio would be of great practical value.

A simple possibility for increasing the sensitivity is the use of cells with a longer path length. However greater scattering losses are

attendant upon the use of such cells, and, in practice, there is nothing to be gained from cells having a path length of more than 3 cm. Hence this approach is capable of not more than a threefold extension of the permissible cadmium to zinc ratio. There is no theoretical reason to doubt the success of this approach but an actual experimental verification was not possible due to lack of the appropriate equipment.

Another alternative would be to operate with a reduced final volume of the chloroform-alcohol solution. It is possible to reduce the quantity of chloroform used in the original extraction and after the backwash step so that a final extract volume of 25 ml results. While this means of obtaining a twofold expansion of the allowable ratio was not carried out in the laboratory for the zinc-cadmium system, its feasibility was demonstrated in the study of the analogous zinc-lead system. Results are presented in Chapter II.

Still another means of achieving the desired end is described next.

Extract Evaporation Procedure

This approach involves a minimal number of additional operations and results in a fivefold gain in the sensitivity. Hence it is applicable to samples having cadmium to zinc molar ratios up to 500,000 to 1.

Directions: Carry out Steps 1 through 9 of the basic procedure. (Note 1). Then clamp the separatory funnel containing the extract in place above a hot plate and evaporate the extract down to a volume of 2 to 4 ml (Note 2). Cool to room temperature (Note 3). Carry out Step 10 of the basic procedure. Drain the organic layer into a 10-ml volumetric flask. Wash

the aqueous phase twice with 1 to 2 ml portions of chloroform and collect the washings in the volumetric flask. Add 2 ml of 95% ethanol. Bring to volume with chloroform. Complete the determination by carrying out steps 13 and 14 of the basic procedure.

Note 1: If the samples are free of extraneous cation interferences, the foregoing procedure can be used in conjunction with the simplified rather than the basic procedure.

Note 2: The use of teflon plug separatory funnels is ideal since teflon acts as a "boiling stone" and eliminates losses from spattering or bumping.

Note 3: The coefficient of thermal expansion of teflon is greater than that of borosilicate glass. Hence there were no problems with losses of liquid between the plug and the stopcock barrel while heating the separatory funnel on the air bath. It follows that there is a potential leakage problem when the vessel cools back to ambient temperature. To avoid such losses it is necessary to increase the tension on the teflon plug at frequent intervals by tightening the nut on the stopcock.

Some results obtained by the application of this procedure to artificial "unknowns" of suitable composition are shown in Table 4.

A different method of attack is described below.

Double Extraction Procedure

This approach differs from the preceeding ones in that, instead

Table 4. Results of the Determination of Zinc in Cadmium Using the Extract Evaporation Procedure. (All runs were made using samples having a cadmium content of 0.90 g. Of the total quantity of zinc taken, 1.0 µg comes from the zinc impurity in the cadmium.)

Quantity of Zinc Taken, Total, µg	Quantity of Zinc Found, µg	Error µg	Error %	Cadmium to Zinc Molar Ratio in Thousands
7.3	6.9	-0.4	- 5	70
7.3	6.7	-0.6	- 8	70
7.3	7.2	-0.1	- 1	70
4.2	3.6	-0.6	-14	120
4.2	3.5	-0.7	-17	120
2.6	2.5	-0.1	- 4	200
2.6	2.6	0	0	200
2.3	1.8	-0.5	-22	230
1.6	2.3	+0.7	+44	330
1.0	1.3	+0.3	+30	520
1.0	1.3	+0.3	+30	520

of attaining the desired goal by increasing the sensitivity, it is designed to get around the limitation of 1 g that is imposed on the cadmium content of the sample. The procedure yields satisfactory results when applied to samples having a cadmium content not exceeding about 2 g. Hence it is capable of handling samples having cadmium to zinc molar ratios of up to 200,000:1.

Directions: Carry out steps 1 through 9 of the basic procedure (Notes 1, 2). Save the aqueous layer remaining after step 9 (Note 3). Repeat steps 6 through 9 with the saved aqueous layer. Collect all the extracts in the same separatory funnel. Complete the determination by carrying out steps 10 through 14 of the basic procedure.

Note 1: If the samples are free of extraneous cation interferences, the foregoing procedure can be used in conjunction with the simplified rather than the basic procedure.

Note 2: The quantity of potassium iodide added in Step 2 must be increased to 13 g of KI per 1 g of cadmium however not less than 20 g must be taken in any event. Increases in the quantity of potassium iodide required that more than the normal volume of water be added in Step 2 in order to dissolve all solids. Consequently the volume of buffer added in Step 4 is increased proportionately.

Note 3: After extracting with the last portion of chloroform great care must be taken to drain all that solvent prior to proceeding to the next operation. If any droplets of chloroform remain in the saved aqueous layer, the PAN added in the

Step 6 of recycle will rapidly enter the chloroform droplets and then fail to react with the zinc remaining in the aqueous medium.

Some results obtained by applying this procedure to artificial "unknowns" of appropriate composition are shown in Table 5. Some disadvantages of this method are the limitation to a twofold increase in the permissible ratio, the increased consumption of costly potassium iodide and the tediousness of the requisite complete separation of chloroform after the first extraction cycle.

Another means of accomplishing precisely what is obtained from the extract evaporation procedure, namely a 10 ml extract volume, is presented in Section 3.2 of Chapter II. It was not applied to the zinc-cadmium system since the same goal is more simply attained by the above mentioned procedure. Its feasibility was demonstrated in the zinc-lead system and results so obtained are shown in Table 12.

All methods of increasing the range at the expense of additional operations lead to some loss of precision due to the extra handling. Furthermore, each approach requires its particular calibration curve because the PAN concentrations in the respective extracts differ from that in the basic procedure. Finally it should be noted that the reduced volume approaches do not lead to smaller errors in the determination of the mass of zinc than does the basic procedure. However these approaches do result in obtaining appreciable absorbances for samples having such a low zinc content that the basic procedure would yield an absorbance only slightly greater than that of the blank.

Table 5. Results of the Determination of Zinc in Cadmium Using the Double Extraction Procedure[1]

Quantity of Cadmium Taken g	Quantity of Zinc Taken, µg	Quantity of Zinc Found, µg	Error µg	Error %	Cadmium to Zinc Molar Ratio in Thousands
1.8	8.3	7.6	-0.7	- 8	130
1.8	8.3	7.6	-0.7	- 8	130
2.7	9.3	7.3	-2.0	-22	170
2.7	9.3	7.8	-1.5	-16	170
3.6	10.3	10.8	+0.5	+ 5	200
3.6	10.3	8.8	-1.5	-15	200
3.6	10.3	7.5	-2.8	-27	200

[1]The quantity of potassium iodide added (Step 2) was increased to 13 g per g of cadmium. Furthermore, as more than the normal volume of water had to be added (Step 2) in order to dissolve all the solids, the volume of maleate buffer added (Step 4) was increased proportionately.

3.8. Study of Samples Containing Interferences

While the focus of this investigation was on the development of a method of determining zinc in high purity cadmium and cadmium salts, an investigation of the effect of diverse ions on the zinc determination was also of interest.

3.8.1. Investigation of Anion Interferences. Some anions were of interest as they are the counter ions in commercially important cadmium salts. Other anions were of interest primarily for their potential use in the masking of cations against PAN. Phosphate was of interest since the possibility of employing a phosphate buffer in place of the maleate buffer was under active consideration.

It was found that quantities well in excess of 1 g of the following species do not interfere: acetate, chloride, nitrate, sulfate and, of course, iodide. It was found that, at least, decigram amounts of the following species are tolerable: carbonate, fluoride, tartrate and thiosulfate. The following species when present in, at least, milligram amounts were found to be acceptable: hexacyanoferrate(II), hexacyanoferrate(III), and thiocyanate. Since no attempts were made to determine the tolerance limits for these anions the actual limits may well be far greater than the permissible amounts indicated above.

Although rather sizable amounts of tartrate were found to be tolerable, even very small amounts of citrate were found to mask zinc against PAN.

Special attention was paid to cyanide as it was desired to use this powerful complexing agent to mask a number of cation interferences against PAN. In systems containing zinc but no cadmium it was found that the tol-

erance limit for cyanide is slightly less than 2 mg. The tolerance of such systems for a quantity of cyanide on the order of a hundredfold molar excess with respect to zinc is surprising. However, if the results of equilibrium calculations made for systems of low ionic strength have any validity in the concentrated potassium iodide medium, in a system buffered at a pH near 7 almost all the cyanide is present as undissociated HCN. In systems in which the cadmium to zinc ratio is large it is probably that the tolerance limit is even greater as the former metal should act as a cyanide "sink."

The tolerance limit for phosphate was found to be about 50 mg. This value was large enough to make possible an investigation of the use of a phosphate buffer in the procedure for determining zinc in a cadmium matrix. The results of such an investigation are presented in Section 3.9.

3.8.2. Investigation of Cation Interferences. Particular attention was paid to those metals likely to be found in high purity cadmium samples. Representative data obtained from the cation interference study are shown in Tables 6 and 7. The results were acquired by application of the basic procedure or, where explicitly noted, slightly modified versions of that procedure to the determination of zinc in test solutions containing zinc, cadmium and one or more other cations of interest.

Stock solutions of known concentration were used in preparing the test solutions. A pipet was used for delivery of the zinc, a measuring cylinder for the cadmium and calibrated droppers for the diverse cations. The zinc content of all the test solutions for which results are shown in Tables 6 and 7 was 26.2 μg however a few additional runs were made

Table 6. Representative Results of the Determination of Zinc in Cadmium in Samples Containing Cation Interferences. (The basic procedure was used. Each sample contained 26.2 µg of zinc. The cadmium content of each sample was 0.90 g, thus the cadmium to zinc molar ratio was 20,000:1.)

Interfering Metal (M)	Quantity of M Present, mg	M:Zinc Molar Ratio	Quantity of Zinc Found, µg	Error µg	Error %
Pb	42	500	26.8	+0.6	+2
Hg in	41	500			
Cu one	13	500			
Ag sample	21	500			
Al	2.2	200			
Pb	42	500	26.3	+0.1	0
Hg in	41	500			
Cu one	13	500			
Al sample	2.8	250			
Ni	1.2	50	26.2	0	0
Co	0.24	10	26.9	+0.7	+3
Bi	4.3	50	27.1	+0.9	+3
Sb	0.60	12	26.8	+0.6	+2
Fe(II)[1]	0.15	7	27.1	+0.9	+3
Fe(III)[1]	0.32	15	26.9	+0.7	+2
Mn	0.022	1	27.5	+1.3	+5
In	0.094	2	26.1	-0.1	0
Ga	0.26	9	26.4	+0.2	+1
Tl(I)	0.71	9	26.5	+0.3	+1
Sn(II)[2]	0.49	10	25.7	-0.5	-2
Sn(IV)	0.049	1	24.6	-1.6	+6

[1]The addition of ascorbic acid was omitted (Step 4).

[2]Using the modified procedure described in the text on page 64.

using test solutions containing other quantities of zinc. The cadmium content of all the test solutions was 0.90 g. Variable known amounts of one or more diverse cations were added.

Interferences are found to fall in one of three groups. Group 1 interferences, when present in sufficient quantity, introduce a positive error, i.e., yield an extract having an absorbance at 556 mμ in excess of that attributable to the amount of zinc panate present. Most of the interfering cations fall in Group 1. The obvious cause of the observed phenomenon is the formation of extractable metal panates having a finite absorptivity at the wavelength of interest. Group 2 interferences cause a negative error. In the maleate buffered systems tin is the only cation found to belong to this group. However if a phosphate buffer is used, several cations are found to produce negative errors. Since some patterns emerged in the course of the work with that buffer rather than in the present system, the presentation of a hypothesis concerning the cause of negative errors is reserved for Section 3.9.2. The presence of Group 3 interferences, thallium being the sole representative observed here, results in the formation of a precipitate. The presence of a precipitate makes it difficult to obtain a clean phase separation after an extraction and errors also result from losses of zinc and zinc panates due to coprecipitation and adsorption.

Experimental data are necessary but not sufficient to establish tolerance limits. The size of the error due to the presence of an interference varies continuously with the amount of the interference. Hence, in order to obtain values for the tolerance limits, some criterion is required for the magnitude of the tolerable error. For Group 1 and Group

2 interferences the tolerance limit is arbitrarily defined as the quantity of interference that results in an error in the absorbance equivalent to 1.0 µg of zinc. Since the presence of a precipitate is, per se, unacceptable, the tolerance limit for the Group 3 interference, thallium, is the consequence of a natural phenomenon rather than an arbitrary definition. The tolerance limits presented in Table 10 are based on the above considerations. In all cases round values are listed and, as these values contain at least some degree of understatement, include a safety factor. The values are based in part on the data shown in Table 6, however many additional runs were required to obtain sufficient information to allow interpolations to be made with confidence.

There is a valid reason for reporting tolerance limits in terms of amounts of interfering species rather than as interference to zinc ratios. Observations made in a limited number of runs using test solutions of differing zinc contents indicate that the former value is a constant. It then must follow that the latter is a variable dependent on the amount of zinc present.

Using the term masking in its most general sense, a portion of the masking of Group 1 and Group 2 interferences in the system under consideration comes about in an interesting and unusual way. The type of masking referred to became apparent only when the standard procedure was applied, in essence, to the determination of zinc in lead. The tolerance limits for Group 1 and Group 2 interferences are considerably less in the lead system. The principal relevant difference between the lead system and the cadmium system is that in the former lead is fully masked against PAN by iodide while in the latter cadmium is only partially masked. Hence

cadmium, which is present in great excess with respect to PAN, serves as a "sink" for that species. The PAN which is bonded to cadmium is kinetically blocked by precipitation. Thus cadmium masks PAN against other cations.

All the data upon which Table 10 is based were obtained with test solutions containing 0.90 g of cadmium. Hence the tolerance limits shown in that table are, strictly speaking, valid only for systems having a cadmium content of 0.90 g. However the procedure is designed for cadmium base samples and when so used there will be present an excess of cadmium with respect to PAN. Thus the tolerance limits will not be particularly sensitive to the cadmium content of the sample.

There is a further restriction upon the applicability of the values of Table 10. A few runs were made with test solutions containing the limiting amounts of two Group 1 cations. The data obtained showed that the tolerance limits are not additive. For instance, the permissible amounts of iron plus manganese in one sample are less than the tolerable limits of iron and of manganese in separate samples. If both antimony and bismuth are present in a single sample, the situation is similar.

No attempt was made to find the interference thresholds for lead, mercury, copper or silver, either alone or in combination in a single sample. The objective of the entire investigation is a method applicable to the determination of zinc in high purity cadmium. However any cadmium sample containing even a fraction of the demonstrated tolerable amounts of these metals would be only 90 per cent or, at best, 99 per cent cadmium. Thus there was no reason to pursue the study to the limit.

The principal purpose of adding sodium thiosulfate and ascorbic

acid in Step 4 of the basic procedure is to reduce any iodine that might result from the air oxidation of iodide. Since iodine is extractable by chloroform and since the resulting extract absorbs radiation at 556 mμ, the presence of iodine is intolerable. In most cases the addition of both of these substances is superfluous since either one alone is sufficient to achieve the desired result, but there is usually no adverse effect attributable to the addition of both. There are, however, some circumstances which require the addition of only one, or of only the other, or of both of these substances. These circumstances occur when dealing with samples containing unusually large amounts of iron, cobalt or copper. These situations are considered next.

Prior to the addition of iodide in Step 2 of the basic procedure any iron present in the sample solution may exist in either of its two common oxidation states or a portion of that species may be present as iron(II) and the remainder as iron(III). The exact situation will depend on the history of the solution. While it might be expected that the addition of a massive amount of iodide would result in the reduction of iron (III) to iron(II) there is evidence to indicate that either the reduction does not occur at the working pH, about 7, or that it occurs only slowly. The pertinent observations are shown below.

Oxidation State of Iron in the Solutions Used to Prepare the Test Solutions	Ascorbic Acid Addition in Step 4 of the Basic Procedure	Tolerance Limit in μg
+3	Omitted	300
+3	Carried out	130
+2	Omitted	130
+2	Carried out	130

Thus it can be seen that if more than about 100 μg of iron are present in a sample, addition of ascorbic acid is counterindicated. Furthermore such samples should be treated in a manner that results in all the iron being present as iron(III). This can be done very simply by the addition of a little nitric acid to the dissolved sample.

The tolerance limit for cobalt drops from 200 μg to less than 20 μg if ascorbic acid is not added. For samples containing significant amounts of cobalt the redundancy may be eliminated if so desired by omitting the addition of sodium thiosulfate but not by omitting the ascorbic acid.

The tolerance limit for copper decreases from a value in excess of 10 mg to about 1 mg if ascorbic acid is not introduced. In samples containing significant quantities of copper, both ascorbic acid and thiosulfate must be applied as a quantity of iodine in excess of that which can be reduced by the added ascorbic acid is produced in the reaction of copper with iodide. The ascorbic acid serves to reduce the minute amounts of copper(II) which remain after equilibrium is attained in the reaction of copper(II) and iodide. Any copper(II) that is present will form interfering panates upon the addition of PAN.

Note that there is an unresolved contradiction between the need to add ascorbic acid if much copper or cobalt are present and the requirement that it be omitted if the system contains much iron. The practical consequences of the contradiction are minimal since pure cadmium samples will not contain the such large amounts of iron, copper and cobalt.

Of the impurities which might be found in high purity cadmium samples the following were expected to react with the cyanide that is added

for masking purposes: cobalt, copper, iron, mercury, nickel and silver. Investigations were made using samples containing these species individually and in various combinations.

Iron(II) and iron(III) both form cyano complexes and as such are masked against PAN however under the conditions of this work only limited amounts of iron can be tolerated. The cyanide content of the system must be restricted in turn in order to avoid any masking of zinc. However, the rapid and complete conversion of iron to hexacyanoferrates is possible only if the ligand is present in sizable excess. Thus the tolerable amount of iron is doubly restricted. If the iron content of the system is large, bluish precipitates of iron hexacyanoferrates are observed. However the tolerance limits for the iron species are far below the precipitation thresholds.

Attempts were made to mask iron(II) with o-phenanthroline and with salicylhydroxamic acid. Attempts were made to mask iron(III) with thiocyanate, sulfosalicylic acid, phosphate, malonate and tiron. For one reason or another none of these reagents achieved the desired result. While only limited amounts of iron are tolerable these amounts considerably exceed the permissible zinc content of the sample. So long as zinc is the main impurity in the cadmium sample, and this is the usual case, there are no difficulties due to the limited tolerance for iron. If an intolerably great amount of iron is present in a particular sample there is the alternative of carrying out a preseparation. One convenient means of so doing is an ether extraction of iron(III) from a hydrochloric acid medium.

The masking of the tolerable amount of iron by cyanide uses up so

little of the ligand, that neither the effect of iron on the cyanide masking of cobalt or nickel nor the effect of cobalt, copper, mercury, nickel or silver on the masking of iron was investigated.

Copper is masked, in the absence of cyanide, by the great excess of iodide already in the system with the added thiosulfate serving to reduce the iodine produced in the reaction between copper(II) and iodide. However, if cyanide is added it is consumed in forming the dicyanocuprate (I) ion which is more stable than are the iodocuprate(I) complexes. As a consequence of the consumption of cyanide by copper, the masking of nickel and cobalt will be affected if they are present in combination with copper. This subject is developed in the discussion of the masking of nickel and cobalt.

The behavior of mercury or silver in the system under consideration is essentially analogous to the behavior of copper. The only noteworthy difference is the absence of redox reaction between these metals and iodide.

If no copper, mercury or silver is present the cyanide masking of nickel takes place without complications. The nickel rapidly reacts with an equivalent amount of the added cyanide to form a complex that is considerably more stable than the cyano complexes of zinc and cadmium. If copper, mercury or silver is present the quantity of cyanide that is available to mask nickel is reduced by the preferential formation of the more stable cyano complexes of the other three metals. The single drop of 1 F potassium cyanide specified in the basic procedure is more than adequate to react with all the copper, mercury, silver and nickel normally present in a portion of high purity cadmium weighing 1 g or less. However

a problem arises if a cadmium sample contains much nickel or any amount of nickel together with a large amount of any or all of the species that form cyano complexes of higher stability. It then becomes necessary to add sufficient cyanide to mask all the nickel without adding so much that the zinc is complexed. A procedure that handles such samples is described in connection with cobalt masking.

Cobalt is masked against PAN by cyanide only if the cyanide to cobalt molar ratio is large. If this ratio is not quite sufficient to achieve total masking of the cobalt a green cobalt(III) panate forms. This species is produced slowly but once formed, is remarkably resistant to decomposition and persists even in the presence of strong acids or cyanide. Its absorptivity at 556 mμ is sufficient to interfere with the photometric determination of zinc. In the solution medium used in the present investigation reducing conditions prevail due to the presence of ascorbic acid, thiosulfate and a great excess of iodide. Yet even under these conditions cobalt(II) is oxidized to cobalt(III) in the presence of PAN. No explanation is offered here. In fact, although several workers in this laboratory have considered the mechanism of the formation of this panate in relatively simple systems, a complete understanding of the process has yet to be attained. As the cyanide to cobalt ratio is further decreased the quantity of interfering green cobalt(III) panate increases and a dark precipitate is also formed in the media employed in the investigation, that is, in the presence of iodide and maleic acid-maleate. The precipitate is produced in such quantities as to make it impossible to complete the determination.

If copper, mercury, nickel and silver are present alone or in com-

bination along with cobalt in the amounts normally anticipated in 1 g or less of high purity cadmium, the specified 1 drop of 1 F potassium cyanide of the basic procedure is sufficient to mask all five of these cations against PAN. But if the sum of the amounts of these species is abnormally high, the quantity of cyanide bound to copper, mercury, nickel and silver, each of which reacts much more rapidly than does cobalt, reduces the effective cyanide to cobalt molar ratio to such an extent that the formation of the interfering green cobalt panate is no longer prevented. It is not necessary to anticipate this undesirable situation since its occurrence is self-evident. Hence it is unnecessary to have foreknowledge of the cobalt, copper, mercury, nickel and silver content of the cadmium sample. The presence of the green species in the extract along with the red panates of the other metals and the yellow of free PAN imparts a brownish tint to the chloroform solutions. This brown is distinctly different from the normal orange color of cobalt-free extracts and provides a clear indication of the fact that cobalt has not been completely masked by the quantity of cyanide present. The cobalt(III) panate, once formed, is either very stable or kinetically inert. Thus if more cyanide is added to the system containing the green panate the cobalt interference is not eliminated and, in addition, zinc is partially masked. A procedure which uses the formation of the green cobalt(III) panate as an indicator in determining the cyanide "equivalent" of an impure cadmium sample is described below.

Additional Cyanide Masking Procedure

The procedure is applicable to cadmium samples containing at least

some cobalt. Its use is necessary for samples containing large amounts of cobalt alone or large amounts of cobalt plus nickel. Its use is also necessary for samples containing any amounts of cobalt or nickel if large amounts of one or more of the following are present: copper, mercury and silver.

Step 1: Proceed as in Step 1 of the basic procedure however modify the final operation of that step as follows: Transfer two aliquots to two separate beakers.

Step 2: Treat each of the aliquots as directed in Steps 2 through 4 of the basic procedure however modify Step 4 as follows: Add no potassium cyanide.

Step 3: Reserve one of the treated aliquots for the zinc determination.

Step 4: Transfer the second treated aliquot to a 50-ml graduated cylinder and add water to bring the volume to 40 ml. This solution is referred to as the working solutions.

Step 5: Transfer a 4 ml portion of the working solution to a test tube. Then, in the order given, add 1 drop of 1 F potassium cyanide, shake, add a few drops of PAN and shake again. Observe the solution after waiting not less than 30 seconds and not more than 5 minutes. If the solution is red or orange proceed to Step 6. If the solution is green or brown repeat the operations of Step 5 with a fresh 4 ml portion of the working solution but add more than 1 drop of 1 F potassium cyanide (Note 1). Continue the operations of Step 5 with fresh portions of working solution until the number of drops of 1 F potassium cyanide needed to prevent the solution from turning green or brown is

determined to the nearest drop. Then proceed to Step 6.

Step 6: Proceed as in Step 5 but now add 0.1 F potassium cyanide instead of 1 F. From Step 5 the number of drops of 0.1 F potassium cyanide needed to prevent the solution from turning green or brown is known to the nearest 10 drops. Now determine this value for 0.1 F potassium cyanide to ± 10 per cent.

Step 7: Add 12 times the number of drops of 0.1 F potassium cyanide determined in Step 6 to the reserved treated aliquot (Notes 2,3). Then, with that solution, complete the zinc determination by carrying out Steps 5 through 14 of the basic procedure.

Note 1: Fewer repetitions are required if the minimum number of drops of the cyanide solution needed to prevent the solution from turning green or brown is obtained from a bracketing process rather if it is approached exclusively from either the low side or the high side.

Note 2: Taking into consideration that the number of drops determined in Step 6 is for a 4 ml portion of the working solution, the treated reserved aliquot might appear to require only 10 times that value. However a slightly greater amount is needed, namely 11 to 13 times the value determined in Step 6.

Note 3: If the number of drops required is sufficiently great it is permissible to use an equivalent amount of a more concentrated solution of potassium cyanide, however the tolerances stated in Step 6 and Note 2 must not be exceeded.

Representative results obtained when using this approach are listed in Table 7. Note that the precision attained is lower than that with sam-

Table 7. Representative Results of the Determination of Zinc in Cadmium in Samples Containing Cation Interferences Using the Additional Cyanide Masking Procedure. (Each sample contained 26.2 µg of zinc. The cadmium content of each sample was 0.90 g, thus the cadmium to zinc molar ratio was 20,000:1.)

Sample Number	Interfering Ions, M	Quantity of M Present, mg	M:Zinc Molar Ratio	Quantity of Zinc Found, µg	Error µg	Error %
1	Pb	42	500	26.1	-0.1	0
	Hg	41	500			
	Cu	13	500			
	Al	2.2	200			
	Ni	1.2	50			
	Co	0.24	10			
2	Pb	42	500	26.4	+0.2	+1
	Hg	41	500			
	Cu	13	500			
	Al	2.2	200			
	Ni	2.4	100			
	Co	1.2	50			
3	Pb	42	500	28.0	+1.8	+7
	Hg	41	500			
	Al	2.2	200			
	Co	1.7	70			
4	Pb	42	500	26.9	+0.7	+3
	Hg	41	500			
	Cu	5.7	220			
	Al	2.2	200			
	Ni	2.4	100			
	Co	2.2	90			
5	Cu	5.7	220	28.1	+1.9	+7
	Ni	2.4	100			
	Co	2.2	90			

Table 7. (Continued)

Sample Number	Interfering Ions, M	Quantity of M Present, mg	M:Zinc Molar Ratio	Quantity of Zinc Found, µg	Error µg	Error %
6	Pb	42	500	26.9	+0.7	+3
	Hg	41	500			
	Al	2.2	200			
	Co	1.7	70			
7	Pb	42	500	25.5	-0.7	-3
	Hg	41	500			
	Cu	8.6	330			
	Al	2.2	200			
	Ni	2.4	100			
	Co	2.2	90			
8	Pb	42	500	28.2	+2.0	+8
	Hg	41	500			
	Al	2.2	200			
	Ni	2.4	100			
	Co	2.2	90			
9	Pb	42	500	25.1	-1.1	-4
	Hg	41	500			
	Cu	13	500			
	Ag	21	500			
	Al	2.2	200			
	Ni	2.4	100			
	Co	1.9	80			

ples not containing unusually large amounts of metals that react with cyanide. Errors of as much as ± 10 per cent may be found. A negative error occurs if too much cyanide is added because then zinc is partially masked. A positive error occurs if too little cyanide is added because nickel or cobalt are then not fully masked. Since the cyano complexes of the interferences are much more stable than the cyano complexes of zinc or cadmium, and since the excess of cadmium serves as a cyanide sink, acceptable results are obtained when the quantity of cyanide to be added is determined with only a low precision.

If a cadmium sample contains no cobalt but does contain some nickel and uncommonly large amounts of one or more of the aforementioned cyanide bonding species more than 1 drop of 1 F potassium cyanide will be required for masking the nickel. This situation can be handled by adding a small quantity of cobalt salt to the dissolved sample. Then it becomes possible to use the additional cyanide masking procedure just described to determine the requisite quantity of that species to be added.

There is no need to determine the cyanide equivalent of solutions containing much copper, mercury and/or silver if these solutions are free of cobalt and nickel. The basic procedure which calls for 1 drop of 1 F potassium cyanide is followed and, as noted earlier, the excess iodide that is present masks the portions of these metals that are not masked by cyanide.

Putting aside the matter of how, or even whether, it is possible to obtain a natural sample solution containing tin(II), a test solution containing that species was investigated. When a drop of PAN is added to that system a colorless solution results. Furthermore, the conversion of

PAN to a colorless species is reasonably rapid. As more PAN is added dropwise the color fading is repeated until eventually a drop is added which imparts a color lasting for at least 20 or 30 seconds. The tolerance limit for tin(II) was determined by carrying out the basic procedure except that Step 6 was modified as follows:

> Add 1 x 10^{-2} F PAN in 95% ethanol dropwise until a color lasting for at least 20 to 30 seconds is imparted to the solution. Then add 0.7 ml of PAN in increments of 0.1, 0.1, 0.1, 0.1 and 0.3 ml. Shake for 2 to 5 seconds after adding each 0.1 ml increment and for 45 seconds after adding the final increment.

Both tin(II)- and tin(IV)-containing solutions produce negative errors however the tolerance limit for tin(II) is much greater than the tolerance limit for tin(IV). A reasonable explanation is possible for some of the various observations noted here. Tin(II) appears to reduce PAN to some colorless species however the reaction is incomplete in that only a portion of the tin(II) originally present is oxidized to tin(IV). Tin(II) itself in moderate amounts does not interfere with the zinc determination but the tin(IV) produced in the redox reaction with PAN does interfere. In phosphate-free systems the observed negative error is characteristic of tin(IV).

Unfortunately no means was discovered to take advantage of the greater tolerance limit of tin(II). Ascorbic acid fails to reduce tin(IV) to tin(II) since the tolerance limit for test solutions prepared with tin(IV) was very low whether or not ascorbic acid was added in Step 4.

While the original objective of the investigation was the development of a procedure applicable to the determination of zinc in high purity

cadmium, the outcome was a method that is both sensitive and highly selective. Thus it is applicable to the determination of zinc in cadmium matrices of almost any purity.

3.9. Additional Investigations (Phosphate Buffer)

The information obtained in the course of the anion interference study indicated that it might be feasible to use a phosphate buffer in place of the maleate buffer. The tolerance limit of phosphate was about 50 mg which corresponds to about 10 ml of 0.05 F phosphate solution.

There were obvious advantages to the use of a phosphate buffer. The reagents needed to prepare phosphate buffers are more commonly found in laboratories, are cheaper and are more readily obtained in higher purity than maleic acid and maleate salts. Furthermore phosphate buffers have a greater buffer capacity at pH 7 than maleate buffers of the same pH and concentration. Once the beneficial effects of cyanide were discovered the formation of interfering interfacial material was no longer a major problem, nevertheless it was possible that the use of a phosphate buffer would completely eliminate the trouble by getting at its source.

3.9.1. Study of Samples Containing Only Zinc and Cadmium in the Presence of Phosphate. A quantitative investigation was begun using artificial "unknown" solutions containing both zinc and cadmium but no other metals which react with PAN. The preparation of the artificial "unknowns" was precisely as described in Section 3.5.

The basic procedure was used except that in Step 4 and in the preparation of the backwash solution (Note 8) 0.08 F phosphate buffer, pH 7.2 was substituted for the maleate buffer on an equal volume basis. The results of this phase of the investigation are shown in Table 8.

Table 8. Results of the Determination of Zinc in Cadmium Using a Phosphate Buffer in Conjunction with the Basic Procedure [1]

Quantity of Cadmium Taken, g	Quantity of Zinc Taken, µg	Quantity of Zinc Found, µg	Error µg	Error %	Cadmium to Zinc Molar Ratio in Thousands
0.22	12.8	12.5	-0.3	-2	10
0.22	25.4	26.3	+0.9	+3	5
0.22	50.6	49.5	-1.1	-2	2.5
0.90	13.6	12.7	-0.9	-7	40
0.90	26.2	25.7	-0.5	-2	20
0.90	26.2	26.2	0	0	20
0.90	26.2	25.8	-0.4	-2	20
0.90	51.4	51.0	-0.4	-1	10

The standard deviation of the error, in µg, is 0.7.

[1] A phosphate buffer was used in place of the maleate buffer.

The range of the determination was extended by use of the extract evaporation procedure described in Section 3.7. The results of this phase of the work are shown in Table 9.

From the data presented in Tables 8 and 9 it is clear that the phosphate buffer and the maleate buffer yield results of comparable quality when applied to the determination of zinc in cadmium in the absence of other interferences.

3.9.2. Interference Studies. A quantitative investigation was begun using test solutions containing 0.90 g of cadmium, 26.2 μg of zinc and suitable amounts of one or more additional cations of interest. The preparation of the test solutions was precisely as described in Section 3.8.2.

The basic procedure was used except that in Step 4 and in the preparation of the backwash solution (Note 8) 0.08 F phosphate buffer, pH 7.2, was substituted for the maleate buffer on an equal volume basis.

Tolerance limits based on the results of this work are shown in Table 10. Inspection of the data presented in the table reveals that, for species other than the precipitate-forming thallium(I), the tolerance limits in the presence of phosphate are markedly lower than those for the maleate buffered system. While in most cases the decrease is between twofold and tenfold, for bismuth it is a hundredfold and for aluminum a thousandfold. It is not obvious from the values that are listed but the tolerance limits of mercury, lead, copper and silver are also lowered. An intolerable interference was observed when zinc is determined in a test solution containing the same quantities of these four species in combination that yield satisfactory results when a maleate buffer is used. Fur-

Table 9. Results of the Determination of Zinc in Cadmium Using a Phosphate Buffer in Conjunction with the Extract Evaporation Procedure.[1] (All runs were made using samples having a cadmium content of 0.90 g. Of the total quantity of zinc taken, 1.0 µg comes from the zinc impurity in the cadmium.)

Quantity of Zinc Taken, µg	Quantity of Zinc Found, µg	Error µg	Error %	Cadmium to Zinc Molar Ratio in Thousands
7.3	6.7	-0.6	- 8	70
5.8	5.3	-0.5	- 9	90
4.2	3.7	-0.5	-12	120
2.6	2.2	-0.4	-15	200
1.0	0.7	-0.3	-30	520

[1]A phosphate buffer was used in place of the maleate buffer.

Table 10. Tolerance Limits of Various Species in The Determination of Zinc in Cadmium. (Samples contained 0.90 g of cadmium. The basic procedure with maleate and with phosphate buffers was used.)

Interference	Tolerance Limit	
	Maleate Buffer	Phosphate Buffer
Hg	>> 40 mg	> 40 mg
Pb	>> 40 mg	> 40 mg
Cu	>> 10 mg	> 10 mg
Ag	>> 20 mg	> 20 mg
Al	2.5 mg	<< 10 µg
Fe(II)	130 µg	70 µg
Fe(III)[1]	300 µg	100 µg
Ni	1.2 mg[2]	not determined[3]
Co	200 µg[2]	not determined[3]
Sb	600 µg	50 µg
Bi	4 mg	50 µg
Ga	300 µg	60 µg
In	100 µg	<< 20 µg
Tl(I)	700 µg	1.5 mg
Sn(II)[4]	500 µg	<< 50 µg
Sn(IV)	<< 50 µg	<< 50 µg
Mn	< 20 µg	< 20 µg

[1]The addition of ascorbic acid was omitted (Step 4).

[2]By the use of the modified procedure described on pages 58-60, the tolerance limits of nickel and cobalt can be increased to about 2.5 mg and 2 mg, respectively.

[3]A positive error was observed when the modified procedure described on pages 58-60 was used with a test solution containing 1.8 mg of Ni and 1.6 mg of cobalt. This positive error persisted even when the amount of cyanide was increased by 20 per cent.

[4]Using the modified procedure described on page 64.

thermore a restricted number of runs indicated that in the phosphate buffered system the tolerance limits are extremely sensitive to small changes in pH, increasing with increases in pH. In the maleate buffered systems the tolerance limits are insensitive to pH variations of, at least, ±0.2 pH units.

It was also observed that in the phosphate buffered system the mode of interference of the following species is the occurrence of a negative error: Al, Ga, In, Fe(II), Fe(III), Sn(II) and Sn(IV). Of the interferences considered in the maleate buffered system only tin introduces a negative error.

A reasonable hypothesis is proposed which accounts for a number of the observations. The negative errors, the decreased tolerance limits and the pH sensitivity all involve species having an oxidation state greater than (plus) two, Fe(II) excepted. (The previously mentioned PAN oxidation of Sn(II) accounts for the fact that Sn(II) is not listed as an exception along with the lower oxidation state of iron.) Since the chelation of the trivalent or tetravalent species by, at most, two uninegative PAN anions is insufficient to produce an unchanged species extractable by chloroform these metal panates must extract as ion association complexes. Even a divalent cation, e.g., Fe(II), may extract an an ion association complex in only one PAN is chelated to it. Furthermore, all these metals form phosphate complexes in preference to iodide complexes. It is proposed that these species are extracted, in the phosphate buffered system, as ion association complexes carrying a sufficient number of dihydrogenphosphate ions to neutralize the portion of the positive charge not neutralized by the chelated uninegative PAN anions. The ex-

traction of an entity capable of acting as a proton donor may affect the "pH" of the chloroform layer and, by lowering this value, cause the zinc panates to decompose and the zinc to backtransfer. Since as was noted earlier, the successful extraction of zinc panates depends on favorable kinetics to overcome the unfavorable equilibrium situation, this system is likely to be particularly sensitive to changes in the "pH" of the organic medium. The extent to which the tolerance limit of aluminum is reduced in the presence of phosphate is striking. Since aluminum strongly prefers phosphate to iodide this observation supports the line of reasoning advanced here.

If the foregoing argument is valid then bismuth and antimony are also extracted as ion association complexes. However the counterion here is likely to be iodide rather than protonated phosphate since these two metals form relatively stable iodo complexes. Hence the presence of bismuth and antimony would not be expected to cause negative errors and experimental observations agree with the expectation. It is admitted that the proposed hypothesis fails to explain the lowered tolerances for these and other metals that do not introduce negative errors.

Regardless of the explanations proffered, it is indisputable that the use of a phosphate buffer is permissible in the determination of zinc in cadmium only if negligible amounts of additional interferences are present.

CHAPTER II

THE DETERMINATION OF ZINC IN THE PRESENCE OF GREAT EXCESSES OF LEAD OR SOME OTHER METALS

1. Introductory Remarks

The success of the method described in the preceding chapter, and the finding that lead, copper, mercury and silver had very high interference thresholds suggested that the approach be applied to the determination of traces of zinc in these metals. Since zinc is commonly found as an impurity in two of these metals, lead and copper, the development of a sensitive and highly selective method for determining zinc in lead or copper matrices would be of practical value and not merely an academic exercise.

2. Experimental

The contents of Section 3.2 of Chapter I apply here with the exceptions and amplifications noted below. All absorbance measurements were made using a Bausch and Lomb Spectronic 20 Spectrophotometer. Stock solutions of the principal cations were prepared using "Baker Analyzed" grades of the following reagents: lead nitrate, copper(II) nitrate trihydrate, mercury(II) chloride and silver nitrate. The lead and copper stock solutions were each 0.50 F in their respective cation species. The mercury stock solution was 0.25 F in mercury and the silver stock solution was 1.0 F in silver.

3. Determination of Zinc in Lead

Lead samples are more likely to contain zinc impurities than copper samples, hence it was decided to begin this phase of the investigation by considering lead systems.

3.1. Preliminary Investigations

Many of the pertinent properties of lead are similar to those of cadmium. Lead forms an intensely colored red panate that is insoluble in water but extractable into chloroform. The panate forms in weakly acidic or neutral media however the presence of excess iodide masks lead against PAN in this pH region.

Per cent extraction vs. pH data *(8, 13, 17)* indicates that the lead and cadmium panates are of comparable stabilities. Furthermore the values of the stepwise formation constants of the iodo complexes of lead and cadmium *(10)* are approximately equal. Hence the findings with respect to iodide masking are precisely as expected.

However there is also one major difference between the lead and cadmium systems. Lead panates were found to resist decomposition for, at least, several minutes in the course of their chloroform extraction from a concentrated potassium iodide medium buffered at a pH of about 7. A brief backwashing with a similar medium also had no noticable effect on lead panates. The possibility of a slow decomposition of lead panates in these operations was not investigated. Even if such is the case, no advantageous use could be made of the phenomenon since zinc panates had been observed to decompose slowly under the specified conditions. In the cadmium system it was necessary and sufficient that there be partial masking of that metal by iodide against PAN; necessary in order to allow a

satisfactorily large fraction of the zinc present to acquire PAN when competing for that substance with cadmium and sufficient because any cadmium panates that do form are decomposed rapidly during the chloroform extraction and in the course of the backwashing. In the lead system it would be necessary to maintain a large enough iodide to lead ratio to fully mask that metal against PAN. Depending upon the amount of lead present and the volume of the solution, 6 to 7 g of potassium iodide are required for each 0.1 g of lead.

Lead iodide differs from cadmium iodide in that the former is only sparingly soluble in water. However the lead iodide precipitate initially formed when potassium iodide is added to a concentrated lead solution dissolves in a sufficient excess of iodide. For the sake of completeness mention is made of the minimum potassium iodide to lead ratios that are needed to prevent the formation of interfering precipitates in the course of the procedure about to be developed. If the volume of the system is not unduly large only about 5 g of potassium iodide are required for each 0.1 g of lead in order to avoid the formation of a precipitate. This value takes into account that the dissolving of potassium iodide is highly endothermic and that the solubility of lead iodide in excess potassium iodide is greatly reduced at low temperature. However at a later step, namely, after the aqueous phase containing zinc panates is shaken with chloroform, it is necessary to add a considerable amount of water in order to lower the density of the aqueous phase and thus permit the separation of the chloroform phase. From this diluted medium, lead iodide slowly precipitates unless the solution is warmed or unless the potassium iodide to lead ratio exceeds 5 g for each 0.1 g of lead. The exact ratio that is needed in the cold solution was not determined, however under all reasonable conditions of temperature and volume it is less than 6 g for each

0.1 g. Thus it is seen that these ratios are all smaller than the 6 to 7 g of potassium iodide for each 0.1 g lead ratio required to completely mask lead against PAN. Hence when that ratio is used no problems related to the formation of precipitates occur.

Since the lead had to be fully masked against PAN it was hoped that backwashing would not be required. When this matter was investigated it was found that backwashing was necessary even for samples containing only zinc and lead. When the layers were separated after extraction tiny droplets of the aqueous phase were found to be trapped in the organic layer. The lead concentration in the aqueous medium was high hence even the tiny amount of that medium which ended up in the organic phase contained lead in an amount that was not negligible in comparison with the quantity of zinc panate extracted. Upon addition of ethanol to the extract the lead present was converted to interfering panates. As previously mentioned it was not feasible to operate without the addition of alcohol since ethanol free extracts were likely to be turbid due to the presence of water droplets.

3.2. Procedures

Using the information acquired in the preliminary investigations the procedures used for the determination of zinc in cadmium were modified to adapt them to the determination of zinc in lead.

The basic procedure is suitable for application to lead or lead salt samples having a zinc to lead molar ratio not exceeding 50,000:1 or a weight ratio not exceeding 160,000:1. Furthermore the lead content of the samples must not exceed about 0.5 g and the zinc content must not exceed about 25 µg.

The ruggedness of the procedure was not investigated but observations on that matter made in connection with the procedure to determine zinc in cadmium are expected to be valid here.

The basic procedure is capable of handling samples containing a number of extraneous cations. The tolerance limits for these cations are found in Table 14.

Basic Procedure

Step 1. Place the sample in a volumetric flask and add the minimum amount of water or, if necessary, hydrochloric or nitric acid required to dissolve the sample. Make up to volume with water. Transfer an aliquot of suitable size to a 50 ml beaker (Note 1).

Step 2. Add 1 ml of tartrate solution of pH 6.8. For each 0.1 g of lead add 10 g of potassium iodide (Note 2). Then add sufficient water to dissolve all solids (Note 3).

Step 3. Immerse the electrodes of a pH meter in the solution and add sodium hydroxide or hydrochloric or nitric acid as necessary until a meter reading of about 7 is obtained.

Step 4. Add 2 ml of 1 F sodium thiosulfate and a spatula tip of ascorbic acid (Note 4). Add 1 drop of 1 F potassium cyanide. Add 5 ml of maleic acid-maleate buffer (Note 5). Now proceed without undue delay.

Step 5. Transfer the solution to a 60 or 125 ml separatory funnel equipped with a teflon stopcock.

Step 6. Add 1.4 ml of 1 x 10^{-2} F PAN in 95% ethanol in increments of 0.2, 0.2, 0.2, 0.2 and 0.6 ml. Shake for 2 to 5 seconds after adding

each 0.2 ml increment and for 45 seconds after adding the final increment.

Step 7. Add 3 to 4 ml of chloroform and shake for 20 seconds. Add water to almost fill the separatory funnel (Note 6) and shake briefly. Allow the phases to separate.

Step 8. Drain the organic layer into a second separatory funnel, the stem and stopcock bore of which must be free of water.

Step 9. Extract the aqueous layer remaining in the first separatory funnel with five 1 to 2 ml portions of chloroform (Note 7). Collect all the extracts in the second separatory funnel.

Step 10. To the combined chloroform extracts add 10 ml of a previously prepared backwash solution (Note 8) and a spatula tip of ascorbic acid. Shake for 20 seconds. Add water to aid the separation of the layers and shake briefly. Allow the phases to separate.

Step 11. Drain the organic layer into a dry 25-ml volumetric flask. Wash the aqueous phase with two 2 to 3 ml portions of chloroform (Note 7). Collect all the organic phases in the volumetric flask.

Step 12. Add 5 ml of 95% ethanol to the volumetric flask and mix. Allow the system to warm to room temperature and then make up to volume with chloroform (Note 9).

Step 13. Measure the absorbance of the chloroform-ethanol solution in a 1-cm cell using water as the reference. Operate at the wavelength of the absorbance maximum (about 550 mμ)(Note 10).

Step 14. Correct for the absorbance of a blank having the same lead content as the sample (Note 11). An absorbance of the blank curve is obtained by plotting absorbance vs quantity of lead for a series of standard lead nitrate solutions (Note 12) which have been treated as described in Steps 1 through 13 above except that in Step 13 use as a reference the blank containing no lead rather than water.

Step 15. Determine the zinc content of the solution by referring to a calibration curve. The calibration curve is obtained by plotting absorbance vs quantity of zinc for a series of zinc standard solutions which contain no lead and have been treated as described in Steps 1 to 13 above (Note 13).

Note 1. If the composition of the sample and its mode of dissolution are such that Step 3, neutralization, is unnecessary the solution may be transferred directly to the separatory funnel instead of the beaker.

Note 2. If the sample is free of extraneous cationic interferences the amount of potassium iodide to be added may be decreased to 7 grams per 0.1 g of lead.

Note 3. There is some reason to believe that marginally better results are obtained if the solution cooled by the dissolving of the salt is not allowed to warm to ambient temperature before proceeding. There is certainly no reason to lengthen the time of the determination by allowing the solution to warm.

Note 4. The size of the spatula that was employed was such that a spatula tip of ascorbic acid had a mass of between 2 and 4 mg.

Note 5. If the electrodes of a pH meter are immersed in the cold solution which is on hand at this point, the meter should read "pH" 7.1 to 7.3. The discrepancy between this value and the nominal pH value of the buffer, 6.8, stems from the grossly changed conditions (lower temperature and much greater ionic strength). Under these conditions reference is clearly and appropriately made to "meter reading" instead of pH value.

Note 6. In the absence of added water the two phases have approximately equal densities and the layers fail to separate.

Note 7. If the organic phase is colorless after use of less than the specified number of portions of chloroform it is not necessary to continue the treatment with that liquid. Instead, proceed to the next step.

Note 8. Prepare the backwash solution as follows: Place 50 g of potassium iodide, 18 ml of maleic acid-maleate buffer, 5 ml of tartrate solution of pH 6.8, 5 ml of 1 F sodium thiosulfate and water in a beaker that has volume markings. After dissolution is complete add water to bring the solution volume to 100 ml. The backwash solution is stable for weeks or months and may be prepared in advance in large lots.

Note 9. A negative error not exceeding 3 per cent occurs if the solution is made up to volume immediately without waiting for it to warm to ambient temperature.

Note 10. The precise wavelength of the absorbance maximum must be determined empirically for the instrument used. An instrumental parameter, namely the bandpass, is involved because the working

solution contains not one but two species, $Zn(PAN)_2$ and free PAN, which absorb light in the wavelength region of interest. For routine work it is permissible to operate at the wavelength of the absorbance maximum of the species of interest, $Zn(PAN)_2$, which is 556 mμ.

Note 11. For samples having a lead content of 0.2 g or less the absorbance of the blank is negligible and Step 14 may be safely omitted. For samples having a lead content of 0.5 g the absorbance of the blank is equivalent to about 2 μg of zinc.

Note 12. The standard lead nitrate solutions are prepared from reagent grade lead nitrate. It is assumed that the zinc content of reagent grade lead nitrate is negligible.

Note 13. Short cuts and economies are permissible in obtaining the calibration curve. When working with the zinc standard solutions it is permissible to use a total of 10 g of potassium iodide (Step 2) and to omit the backwash operation.

Attention was then directed to the design of one or more procedures applicable to samples having a zinc to lead molar ratio in excess of 50,000:1, the limiting ratio of the standard procedure. The desired end may be achieved by a procedure capable of yielding increased sensitivity or accepting samples with a higher lead content or both. A number of approaches to that end are described in Section 3.7 of Chapter I for the closely related cadmium system. One of these, namely, operation with a 25 ml rather than a 50 ml extract volume, has already been incorporated into the standard procedure for the lead system.

Another approach, namely, double extraction, successfully used in

the cadmium system is of no value here. It does not negate the sample size restriction of the standard procedure because it does not eliminate the problem that arises when the lead content of a sample exceeds about 0.5 g. (See Section 3.3.1. of this Chapter).

The remaining approaches of Section 3.7 of Chapter I should be applicable to the lead system. The use of a 3-cm cell was not investigated experimentally for the reason previously given, namely, no such cell was available. The extract evaporation procedure was not used since the increase in sensitivity would be only a factor or two and a half, bearing in mind that the standard procedure calls for a 25 ml extract volume, and since the feasibility of the approach had already been demonstrated in the cadmium work.

The following procedure was specifically designed for the lead system. It gives increased sensitivity by yielding a 10-ml extract volume and also permits the taking of samples with a lead content exceeding 0.5 g.

Acid Stripping and Reextraction Procedure

The procedure was applied to test solutions having a lead content of 1 g (Note 1) and a lead to zinc molar ratio of 250,000:1. The weight ratio was 800,000:1.

Directions: Carry out Steps 1 through 10 of the basic procedure. Drain the organic layer into a fresh separatory funnel. Wash the aqueous phase with two 2 to 3 ml portions of chloroform. Collect all the organic phases in the separatory funnel. Then add 2.00 ml of 0.100 F hydrochloric acid (Note 2) to the collected organic solution and shake. Discard the or-

ganic layer (Note 3). Add 2 ml of the maleate buffer, 2.00 ml of 0.100 F sodium hydroxide (Note 2), 5 g of potassium iodide and shake. Then carry out Step 6 of the basic procedure. Shake with a 2-ml portion of chloroform. Add water to allow the layers to separate. Drain the organic layer into a 10-ml volumetric flask. Extract the aqueous solution remaining in the separatory funnel with five 1 ml portions of chloroform. To the combined extracts in the volumetric flask add 2 ml of 95 per cent ethanol. Allow the system to warm to room temperature and bring to volume with chloroform. Complete the zinc determination by carrying out Steps 13 through 15 of the basic procedure.

Note 1. There is no obvious theoretical reason that limits the applicability of the procedure to samples having a lead content not exceeding 1 g. However 10 g of potassium iodide are required for each 0.1 g of lead. For economic reasons, the applicability of the procedure has not been demonstrated for samples having a lead content exceeding 1 g.

Note 2. Neither the amount nor the concentration of the hydrochloric acid and the sodium hydroxide must be as specified. However these two solutions must be added in equivalent quantities.

Note 3. Take care to remove all the chloroform droplets.

The above procedure requires standard solutions of acid and base in addition to the usual solutions, and much more operator time is required than in either of the two immediately preceding approaches which also yield increased sensitivity. Obviously the method is indicated only

when the other approaches fail because of an extreme zinc to lead molar ratio in a sample.

3.3. Study of Samples Containing Only Zinc and Lead

A quantitative study was begun of solutions containing both zinc and lead but no other metals which react with PAN. The necessary solutions were prepared by mixing measured volumes of standard zinc and lead stock solutions in appropriate ratios. Pipets or burets were used to deliver the zinc solution and graduated cylinders were employed for the lead solution. Since the stock solutions contained no strong acids neutralization was unnecessary.

3.3.1. Results and Discussion. Table 11 gives the results of a series of runs using the basic procedure.

The principal source of the systematic error here is the presence of some lead panates in the extract. These panates absorb in the wavelength region of interest and introduct a positive error. As will be shown shortly, no other reasonable explanation satisfactorily accounts for the discrepancy between the amount of zinc taken in the form of a standard zinc nitrate solution and the quantity of zinc found.

If only small and reproducible amounts of lead panates are extracted a blank correction can be applied as directed in the basic procedure. It was found that when the lead content of a sample does not exceed about 0.2 g only negligible amounts of lead panates are formed and no blank correction is necessary. At a lead content of about 0.5 g the error is equivalent to 1.8 ± 0.2 μg of zinc and good results can be obtained by a correction. At a lead content of about 1 g the error is equivalent to 6 ± 1 μg of zinc. This blank correction is so large and so imprecise in comparison with the quantity of zinc sought that good results can not be obtained by use of a blank correction. Furthermore it was

Table 11. Results of the Determination of Zinc in Lead Using the Basic Procedure

Quantity of Lead Taken, g	Quantity of Zinc Taken, µg	Quantity of Zinc Found µg	Error µg	Error %	Lead to Zinc Molar Ratio in Thousands
0.21	25.2	25.6	+0.4	+ 2	2.5
		23.9	-1.3	- 5	
		24.6	-0.6	- 2	
		24.1	-1.1	- 4	
0.21	12.6	12.2	-0.4	- 3	5
		12.3	-0.3	- 2	
0.21	6.3	5.7	-0.6	-10	10
		5.9	-0.4	- 6	
0.21	3.1	2.9	-0.2	- 6	20
		3.5	+0.4	+13	
		4.0	+0 9	+29	
0.53	25.2	24.0	-1.2	- 5	6.2
		26.0	+0.8	+ 3	
		26.0	+0.8	+ 3	
0.53	9.4	9.6	+0.2	+ 2	17
		9.4	0	0	
0.53	3.1	2.7	-0.4	-13	50
		2.5	-0.6	-19	
		3.1	0	0	

The mean error is -0.2 µg.

The standard deviation of the error is 0.7 µg.

found that the error persists even when potassium iodide is added in an amount 50 per cent greater than that specified in the standard procedure. It is this error that limits the applicability of the basic procedure to samples with a lead content not exceeding about 0.5 g.

The possibility must be considered that the discrepancy just described is not an error at all but is instead attributable to there being a significant amount of zinc added to the test solutions in the form of a zinc impurity in the lead nitrate. If this were the case, the magnitude of the discrepancy would vary linearly with the size of the lead sample. Since this is not what is observed, the zinc content of the lead nitrate can not be responsible for more than a small fraction of the observed discrepancy. In fact it is satisfactory to assume that the zinc impurity in the lead nitrate is negligible.

The possibility that the presence of some cationic impurity in the lead nitrate is responsible for the discrepancy must also be considered. If this were the case, one or more of the species commonly found as impurities in lead would have a tolerance limit close to zero. As Table 14 shows no such species was found.

It follows from the elimination of the two foregoing possibilities that the discrepancy is attributable, as stated above, to the presence of lead panates in the extract and is, therefore, an error inherent in the procedure.

There is an inherent upper limit imposed on the lead to zinc molar ratio that can be handled by the standard procedure. The limitation on the maximum size of the lead sample has been considered above. The limitation of a minimum permissible amount of zinc comes about for the reasons

stated in Section 3.7 of Chapter I. However the lower limit here is about 3 μg since the extract volume in the lead basic procedure is only half as great as that in the cadmium standard procedure and hence the sensitivity is twice as great. As a consequence of these limitations the standard procedure can handle samples having a lead to zinc molar ratio up to about 50,000:1 or a weight ratio up to about 160,000:1.

The use of the acid stripping and reextraction procedure overcomes the foregoing restrictions, however, several additional operations become necessary and high precision is not to be expected. Only two runs were made using this procedure and the lead content of the samples used was limited to about 1 g for reasons of economics. It will be recalled that the procedure uses potassium iodide, a relatively expensive inorganic reagent, in the amount of 10 g for each 0.1 g of lead. The results of these runs are shown in Table 12.

Table 12. Results of the Determination of Zinc in Leading Using the Acid Stripping and Reextraction Procedure. (In each run the quantity of zinc taken was 1.3 μg. The lead content of each sample was 1.06 g, thus the lead to zinc molar ratio was 250,000:1 and the weight ratio was 800,000:1.)

Run Number	Quantity of Zinc Found μg	Error μg	Error %
1	1.6	+0.3	+23
2	1.8	+0.5	+39

It has been observed throughout the investigation that the magnitude of the absolute error is essentially independent of the zinc content of the sample. Hence samples having a larger zinc content will yield

results that have a smaller per cent error.

3.4. Study of Samples Containing Interferences

A quantitative study was begun of test solutions containing both zinc and lead plus one or more other ions of interest. A few anions were considered. These were the counterions in some commercially important lead salts. A number of cations were investigated and particular attention was given to those likely to be found in high purity lead.

The test solutions were prepared by mixing measured volumes of standard zinc and lead stock solutions in appropriate ratios and adding suitable volumes of standard solutions containing the other ions of interest. Pipets were used to deliver the zinc solution, graduate cylinders were used for the lead solution and calibrated droppers were employed for the diverse ions.

Representative data obtained from the interference study are shown in Table 13. The basic procedure was used for almost all of the runs. Slight modifications of that procedure were used in the study of iron(III) and tin(II) as noted in the table. A few runs were made employing the approach of additional cyanide masking as described in Section 3.8.2 of Chapter I.

As in the cadmium system the cations other than tin and thallium fall in interference Group I, that is, their presence introduces a positive error. As will be elaborated upon shortly, some of the members of Group I produce a positive interference in an indirect way rather than by forming panates themselves Tin causes a negative error (Group 2) and thallium forms a precipitate (Group 3). One anion, sulfate, also interferes by precipitate formation.

Table 13. Representative Results of the Determination of Zinc in Lead in Samples Containing Interferences. (The standard procedure was used unless explicitly noted. Each sample contained 4.0 µg of zinc. The lead content of each sample was 0.25 g, thus the lead to zinc molar ratio was 20,000:1.)

Interference	Quantity of Interference Present, mg	Interference to Zinc Molar Ratio	Quantity of Zinc Found, µg	Error µg	Error %
Acetate	540	150,000	3.8	-0.2	- 5
Sulfate	260	44,000	3.6	-0.4	-10
Chloride	190	130,000	3.6	-0.4	-10
Cd	25	3,600	4.4	+0.4	+10
Cu	3.0	750	4.3	+0.3	+ 7
Hg(II)	19	1,600	4.3	+0.3	+ 7
Ag	7.2	1,100	3.9	-0.1	- 3
Au(III)	5.2	430	4.3	+0.3	+ 7
Al	1.3	750	4.1	+0.1	+ 3
Ga	0.085	20	4.3	+0.3	+ 7
In	0.035	5	4.4	+0.4	+10
Tl(I)	1.7	140	3.8	-0.2	- 5
Sb	0.150	20	4.1	+0.1	+ 2
Bi	0.380	30	3.9	-0.1	- 3
Fe(III)	0.085	25	3.9	-0.1	- 2
Fe(III)[1]	0.035	10	3.7	-0.3	- 7
Fe(II)	0.035	10	3.8	-0.2	- 5
Co	0.140	40	4.4	+0.4	+10
Ni	0.230	65	3.9	-0.1	- 3
Mn	0.020	6	4.2	+0.2	+ 5
Sn(II)[2]	0.060	8	4.1	+0.1	+ 2
Sn(IV)	0.012	2	3.5	-0.5	-13

Table 13. (Continued)

Interference	Quantity of Interference Present, mg	Interference to Zinc Molar Ratio	Quantity of Zinc Found, µg	Error µg	Error %
Cd	12	1,800			
Cu	0.8	200	in one sample	+0.1	+ 2
Hg	2	160	4.1		
Ag	0.9	140			
Cd	24	3,600			
Cu	1.6	400	in one sample	+1.0	+25
Hg	4	320	5.0		
Ag	1.8	280			
Cd	25	3,600			
Cu	6	1,500			
Hg(II)	19	1,600	in one sample[3]	+0.8	+20
Ag	7.2	1,100	4.8		
Co	1.7	500			
Ni	0.7	200			
Cd	38	5,400			
Cu	6	1,500			
Hg(II)	38	3,200	in one sample[3]	+1.2	+30
Ag	18	2,500	5.2		
Co	1.7	500			
Ni	0.7	200			
Cd	25	3,600			
Cu	6	1,500			
Hg(II)	19	1,600	in one sample[3]	+1.6	+40
Ag	7.2	1,100	6.4		
Co	1.7	500			
Ni	0.7	200			
Au(III)	10	850			

Table 13. (Continued)

1. The addition of ascorbic acid was omitted (Step 4).

2. Using the modified procedure described in the text on page 64.

3. Using the additional cyanide masking procedure in conjunction with the standard procedure for lead systems.

For all the Group 1 and Group 2 cations the interferences thresholds are considerably lower in the lead system than in the cadmium system. This significant difference can be explained as follows. As was previously stated, lead panates do not decompose to an appreciable extent during the extraction or the backwashing. Hence, lead had to be fully masked by iodide against PAN and thus, unlike cadmium, lead fails to act as a PAN "sink."

The most striking decreases in the interference thresholds are for the species that form relatively stable iodo complexes, namely, copper, mercury and silver. In the cadmium system the interference thresholds for these species were so high that no attempt was made to determine them. However in the lead system these cations, along with cadmium, have readily detectable interference thresholds even though none of these cations form panates that are extracted when the standard procedure is carried out. Instead they tie up iodide and prevent the complete masking of lead against PAN. Hence the positive error results directly from the presence of lead panates and only indirectly from the cadmium, copper, mercury or silver. In a strict sense these cations comprise a subgroup of the Group 1 interferences. The use of a greater potassium iodide to lead ratio would be expected to raise the interference thresholds of these cations. No investigations were made employing a higher iodide to lead ratio since the observed thresholds were more than adequate for zinc determinations in lead of even moderately high purity.

As is shown in Table 13 only moderate increases in the tolerance limits results from use of the approach of additional cyanide masking in conjunction with the basic procedure for lead systems.

The tolerance limits for the diverse ions considered are shown in Table 14. As mentioned in Section 3.8.2 of Chapter I, the definition of the tolerance limit is arbitrary except cases where a precipitate is involved. The criterion used in Table 14 is that for Group 1 and Group 2 type interferences the listed quantity causes an error that is equivalent to 0.4 μg of zinc. These tolerance limits apply to systems containing 0.25 g of lead, and are expected to be greater for systems containing less lead but smaller for systems having a higher lead content. The round values listed are understated in all cases, hence they contain a built-in safety factor. The values are based in part on the data shown in Table 13, however many additional runs were required to obtain the information necessary to allow interpolations to be made with confidence. As was shown in the work with the closely related cadmium system, the tolerance limits for species in combination in a single sample are not additive. The presentation of tolerance limits in terms of μg of interference rather than in terms of interference to zinc ratio is justified by the observation that the former value is constant and, hence, the latter must be a variable dependent upon the zinc content of a sample.

Although the tolerance limits for Groups 1 and 2 cations are lower here than in the cadmium system they are sufficiently high to readily permit the determination of zinc in high purity lead.

4. The Determination of Zinc in Copper, Mercury or Silver

Only superficial observations were made of the copper, mercury and silver systems. These observations were sufficient to establish the feasibility of iodide masking in these systems, and to estimate the limiting

Table 14. Tolerance Limits of Various Species in the Determination of Zinc in Lead. (Samples contained 0.25 g of lead. The basic procedure was used.)

Interference	Tolerance Limit, mg
Acetate	500
Sulfate	250
Chloride	180
Cd[1]	25
Cu[1]	4
Hg(II)[1]	30
Ag[1]	10
Au(III)	6
Al	3
Ga	0.1
In	0.03
Tl(I)	1.5
Sb	0.2
Bi	0.5
Fe(III)[2]	0.1
Fe(II)	0.05
Co[1]	0.12
Ni[1]	0.25
Mn	0.02
Sn(II)[3]	0.06
Sn(IV)	< 0.01

[1]Moderate increases in the tolerance limits are possible using the approach of additional cyanide masking described in Section 3.8.2 of the preceding chapter in conjunction with the basic procedure of the lead chapter.

[2]The addition of ascorbic acid was omitted (Step 4).

[3]Using the modified procedure described on page 64.

metal to zinc ratios. These values are shown in Table 15. The conditions employed include the presence of 20 g of potassium iodide and an extract volume of 25 ml. In the case of copper, ascorbic acid had to be present.

Table 15. Approximate Limiting Ratios for the Determination of Zinc in the Presence of Great Excesses of Copper, Mercury or Silver.[1]

Matrix Metal	Limiting Metal to Zinc Molar Ratio	Limiting Metal to Zinc Weight Ratio
Copper	50,000:1	50,000:1
Mercury	500,000:1	1,500,000:1
Silver	250,000:1	400,000:1

[1]Using 20 g of potassium iodide and a 25 ml extract volume.

Since these metals form iodo complexes of great stability it is expected that the addition of more than 20 g of potassium iodide would permit the use of larger samples of the metal and would not affect the sensitivity. Thus it would be possible to increase the permissible metal to zinc ratios.

Since silver does not form a panate the function of the iodide that is added in that system is not the masking of silver against PAN. Its function is (a) to prevent the formation of silver precipitates in the working medium used and (b) to increase the selectivity of the method by masking other interfering metals against PAN. It should be noted that zinc does not form an extractable panate in the presence of a high concentration of ammonia, thus an ammonia-ammonium buffer is ruled out as the working medium for this system.

No investigations were made of the tolerance of the copper, mercury or silver systems for extraneous interferences. Since these cations all form high stability iodide complexes the tolerance limits would be expected to be no greater than those of the lead system, and might well be even lower.

APPENDIX

GLOSSARY OF COMMON NAMES AND ABBREVIATIONS

Chelons

DTPA: (diethylenetrinitrilo)pentaacetic acid

EDTA: (ethylenedinitrilo)tetraacetic acid

EGTA: [ethyleneglycolbis(nitriloethyl)]tetraacetic acid

Indicators and Chromogenic Agents

Eriochrome Black T: The sodium salt of 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonate

PAN: 1-(2-pyridylazo)-2-naphthol

PAR: 4-(2-pyridylazo)-resorcinol

Xylenol Orange (XO): 3',3"-bis([bis(carboxymethyl)amino]methyl)-5',5"-dimethylphenolsulfonphthalein

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*Journal title abbreviations are those in "List of Periodicals," *Chemical Abstracts*, 1961.

VITA

Roger Harvey Weiss was born on July 13, 1926, in New York, New York to Morton Weiss and Leah Bellinson Weiss. He attended Baldwin High School and graduated in absentia in June 1944.

In March 1944 he entered the Navy and was sent to Cornell University, Ithaca, New York and the College of the Holy Cross, Worcester, Massachusetts. He was graduated from the latter with a Bachelor of Naval Science, cum laude, in June 1946 and was simultaneously commissioned an ensign in the Navy. After further naval service he reentered Cornell University in September 1948 and was graduated from that school with an A.B. in chemistry in June 1950.

In September, 1950, he began graduate work in chemistry at the University of Minnesota, Minneapolis, Minnesota. While in graduate school he served as a teaching assistant and received a 3M and a DuPont Fellowship. This work was interrupted from September 1954 to September 1957, when he was employed as an instructor of chemistry at the University of Toledo, Toledo, Ohio. He returned to graduate work at the University of Minnesota from September 1957 to September 1959.

In February 1953 he was married to Anne Eleanor Scott of Minneapolis, Minnesota. They are the parents of two sons, David Scott, born in December 1960 and Paul Steven, born in December 1963.

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In the summer of 1964 he was a National Science Foundation Faculty Research Participant under Dr. H. A. Flaschka in the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia. In June 1966 while on sabbatical leave from Humboldt State College, he began graduate work in the School of Chemistry, Georgia Institute of Technology. He was awarded a National Science Foundation Science Faculty Fellowship for the academic year 1967-68.